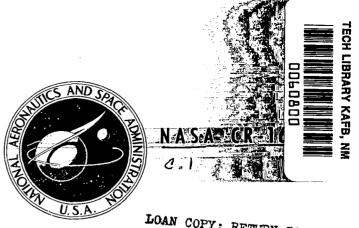
NASA CONTRACTOR REPORT



LOAN COPY: RETURN TO AFWL (WLOL) KIRTLAND AFB, N MEX

OPERATION OF A THERMIONIC CONVERTER WITH A (112) TO (114) ORIENTED TUNGSTEN EMITTER AND A NIOBIUM COLLECTOR WITH OXYGEN PRESENT

by V. C. Wilson and S. P. Podkulski

Prepared by
GENERAL ELECTRIC COMPANY
Schenectady, N. Y.
for Lewis Research Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION . WASHINGTON, D. C. . SEPTEMBER 1970

3. Recipient's Catalog No. 5. Report Date September 1970 6. Performing Organization Code 8. Performing Organization Report No. GESP-9006 10. Work Unit No. 11. Contract or Grant No. NAS 3-8511 13. Type of Report and Period Covered Contractor Report 14. Sponsoring Agency Code				
September 1970 6. Performing Organization Code 8. Performing Organization Report No. GESP-9006 10. Work Unit No. 11. Contract or Grant No. NAS 3-8511 13. Type of Report and Period Covered Contractor Report				
8. Performing Organization Report No. GESP-9006 10. Work Unit No. 11. Contract or Grant No. NAS 3-8511 13. Type of Report and Period Covered Contractor Report				
10. Work Unit No. 11. Contract or Grant No. NAS 3-8511 13. Type of Report and Period Covered Contractor Report				
11. Contract or Grant No. NAS 3-8511 13. Type of Report and Period Covered Contractor Report				
NAS 3-8511 And Period Covered Contractor Report				
NAS 3-8511 A				
13. Type of Report and Period Covered Contractor Report				
14. Sponsoring Agency Code				
14. Sponsoring Agency Code				
I				
A parallel plane, variable spaced, thermionic converter with a fluoride vapor deposited emitter, a niobium collector and a niobium guard ring was built and tested. Current-voltage characteristics were obtained for a range of emitter temperatures from 1670 to 2153 K, collector temperatures from 773 to 1073 K, cesium reservoir temperatures from 513 to 641 K, and spacings from 2 to 20 mils. The results are compared to those of a converter using a polycrystalline tungsten emitter and a niobium collector.				

17. Key Words (Suggested by Author Thermionic converter performance of the Tungsten emitter Niobium collector with con	formance test	18. Distribution Statement Unclassified – unlimited			
19. Security Classif. (of this report) Unclassified	20. Security Class	sif. (of this page) assified	21. No. of Pages 77	22. Price* \$3.00	

•			

FOREWORD

The research described herein, which was conducted by the General Electric Company Research and Development Center, was performed under NASA contract NAS 3-8511 with R. P. Migra, Nuclear Systems Division, NASA Lewis Research Center, as the Project Manager. The report was originally issued as General Electric report GESP-9006.

•			

CONTENTS

	Page
SUMMARY	1
INTRODUCTION	3
TEST VEHICLE	4
PREPARATION OF THE EMITTER SURFACE	6
CONVERTER OPERATION	8
CHARACTERIZATION OF THE ELECTRODES AFTER CONVERTER OPERATION	20
COMPARISON WITH OTHER CONVERTERS	26
DISCUSSION	31
CONCLUSIONS	33
SYMBOLS AND DEFINITIONS	34
REFERENCES	35
APPENDIX A	36

ILLUSTRATIONS

		Page
(1)	Cross Section of the Thermionic Converter	5
(2)	Emitter Work Function Versus Temperature	7
(3)	Change in J-V Curves Caused by Disconnecting the Guard	9
(4)	Performance at $T_F = 1673^{\circ}K$ Before and After Repairing an Envelope Leak	11
(5)	J-V Curves at $T_E = 1673^{\circ}K$ Showing Changes in Output Performance with Time	13
(6)	J-V Curves at T_E = 2153 o K, T_{Cs} = 613 o K and 5-mil Spacing and for Various Collector Temperatures	15
(7)	J-V Curves at $T_E = 1673^{\circ}K$, $T_{Cs} = 527^{\circ}K$, 10-mil Spacing and for Various Collector Temperatures	16
(8)	A Summary of the Output Potential Versus Collector Temperature for Several Emitter Temperatures all at 10 Amperes/cm ² and 5-mil Spacing, Except as Noted	17
(9)	Envelopes of J-V Curves at Various Emitter Temperatures; 5-mil Spacing, T_{Cs} and T_c Optimized	18
(10)	Envelopes of J-V Curves for Various Emitter Temperatures; 10-mil Spacing, T_c and T_{Cs} Optimized	19
(11)	Photograph of the Collector After Converter Operation	21
(12)	Photograph of the Emitter After Converter Operation	21
(13)	Microphotograph of the Emitter, 240X	22
(14)	Map of the Emitter After Converter Operation.	24
(15)	Comparison of Output Performance of Three Converters at 10 Amperes/cm ² and 10-mil Spacing	27
(16)	J-V Curves for the Three Converters of Figure 15 Under Similar Conditions at $T_{\rm E}$ =2153 $^{\rm O}$ K	28
(17)	J-V Curves for the Three Converters of Figure 15 at ${\rm T_E}$ =1673 $^{\rm O}$ K	29

SUMMARY

The converter reported here had adjustable spacing, a fluoride vapor deposited W emitter, a Nb collector, and a Nb guard ring. The collector and guard ring could be maintained at the same temperature and electrical potential. The structure was similar to previous converters tested except for a modification in the emitter support.

The emitter surface was a 0.020-inch-thick layer of fluoride vapor deposited W on a 1/4-inch disk of General Electric weldable grade W. Before assembling the converter, x-ray diffraction tests verified that the emitter surface was (100) oriented W. The work function of the emitter was 4.57 eV at 2200°K. Mounted in the converter, the emitter work function at 2200°K was 4.52 eV and at 2300°K was 4.56 eV. After introducing Cs, the collector had a minimum work function of 1.54 eV, which had further reduced to 1.44 eV at the end of testing.

Difficulties were encountered during the outgassing. However, it was thought that the converter was vacuum tight while the Cs was distilled into the converter. During operation the output characteristics improved, particularly in the first few hours. Upon taking the converter apart, a coating of W and WO₂ was found on the collector and guard. This coating on the collector probably caused a lowering of the $\phi_{\rm C}$ as measured at the end of testing. Also, grain growth had occurred in the emitter so that the exposed emitter surface changed from (100) crystal planes to (112), (113) and (114) crystal planes.

The current density versus voltage curves presented in Appendix A are a complete set taken after more than 100 hours

of operation and after the converter appeared to have moderately stable output performance. Therefore, these J-V curves are assumed to be representative of a W(112) to (114) emitter and a collector of W \pm WO₂ on Nb.

A comparison of the output of this converter with others operated under similar emitter and collector temperatures shows a little higher performance than a converter with a polycrystalline W emitter and a Nb collector, but lower output than two converters with emitters having (110) oriented W surfaces. This converter operated at lower Cs reservoir temperatures than any other tested in this program, a characteristic probably resulting from the presence of O_2 .

INTRODUCTION

The work reported here is part of a program conducted for NASA-Lewis Research Center under Contract NAS 3-8511, Task III. This program consists of building and operating thermionic converters with various electrode materials in order to characterize, evaluate, and identify the most promising electrode surfaces for converter operation. The table below indicates the emitter material, collector material, and spacing for the 12 converters of this series. Converters 7 through 12 in the table cover the NASA-sponsored program (converter 10 is the converter covered in this report). The measured performances are documented in the references listed.

	<u>Emitte</u> r	Collector	Spacing (Inches)	Reference
(1)	Polycrystalline W	Ni	0.005	1
(2)	Polycrystalline Re	Ni	0.005	1
(3)	Polyc r ystalline Re	Ni	0.002	2, 3, 4
(4)	Polyc r ystalline W	Ni	0.002	4,5
(5)	Polycrystalline W	W	0.002	5
(6)	W-25 w/o Re	Ni	0.005	5
(7)	Polyc r ystalline W	Nb	0.001 to 0.020	6,7
(8)	Vapor Deposited (100) W, {110} Etch	Nb	0.001 to 0.020	8
(9)	Vapor Deposited (110) W, {110} Etch	Ni	0.005	9
(10)	Vapor Deposited (112) W	W + WO ₂ on Nb	0.002 to 0.020	-
(11)	Vapor Deposited (110) W	Nb	0.002 to 0.020	*
(12)	Vapor Deposited (110) W	Mo on Nb	0.005 to 0.020	*

^{*}Results to be published.

TEST VEHICLE

Figure 1 shows a cross-section drawing of the thermionic converter. It is similar to that of Reference 8 but with a modification to the support for the emitter. In previous converters, difficulties had been encountered in making a Nb braze of the W emitter to the Ta thin cylinder. In this converter the thin cylinder was made of 0.005-inch-thick W-25 w/o Re alloy, The cylinder was extended up rather than down from the emitter. The W-25 w/o Re cylinder was made by rolling a 0.005-inch-thick foil into a cylinder and vacuum electron beam welding a closure seam. This cylinder was then electron beam welded to the W emitter and to a Mo ring at the upper end. The Mo ring was Cu brazed to a Ni spinning which was beam welded to the large Ni heat radiator and structural member at the top of the device. For a detailed description of the fabrication, assembly, and outgassing, see Appendix A of Reference 7.

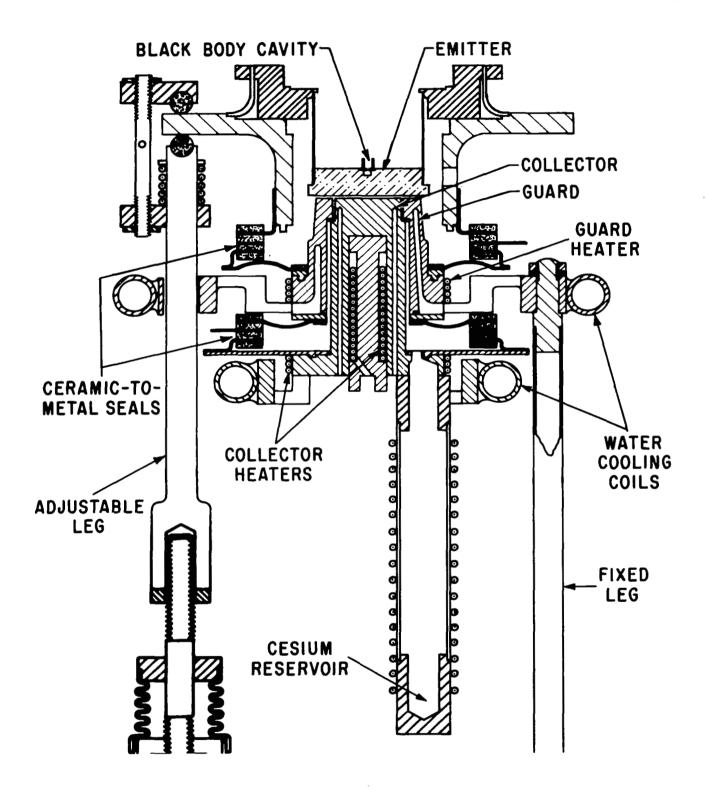


Figure 1. Cross Section of the Thermionic Converter

PREPARATION OF THE EMITTER SURFACE

A 0.250-inch-thick polycrystalline W emitter disk was coated with a 0.020-inch-thick layer of (100) oriented W by fluoride vapor deposition process. After a preliminary polish, a hardness test developed by Festa and Danko $^{(10)}$ indicated that the sample had less than 10 ppm of fluoride in the deposited layer. An x-ray diffraction analysis showed that the sample was highly oriented with the (100) planes parallel to the bulk surface.

The surface was given a final mechanical polish and an electropolish described in Reference 8. Figure 2 shows the work function of this emicer before and after a heat treatment at 2400°C for 30 minutes. The final work function at 2200°K was 4.57 eV.

This converter was plagued with troubles. Three times, while processing the converter, leaks developed in three different places. Finally, in May 1968 the envelope appeared vacuum tight after outgassing. The work function of the emitter was measured just before admitting the Cs. These values are the numbered points in Figure 2. The numbers indicate the order in which the data were taken. The agreement of points 1 and 6 suggest that the work function was not changing during the measurements. The shape of the curve is unusual. At 2200° K, $\phi_{\rm E} = 4.52$ eV.

After introducing the Cs, the minimum work function of the collector was 1.54 eV. This appears low for Cs on Nb. Perhaps during the several outgassing operations some W or WO₂ accumulated on the collector.

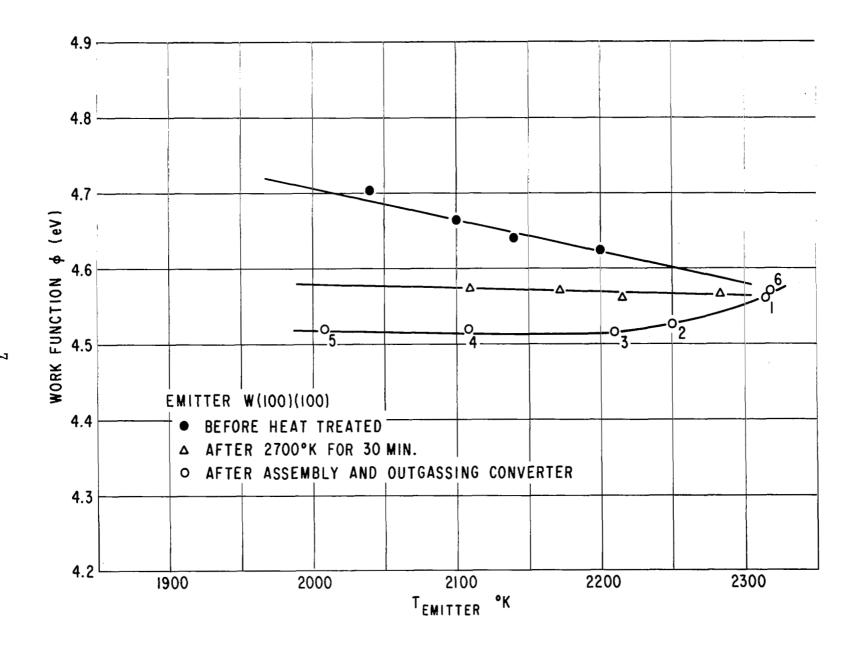


Figure 2. Emitter Work Function Versus Temperature

CONVERTER OPERATION

The first variable spaced converter (VG-12) of this series (6,7) did not have a guard ring. In reporting on this converter (7) we asserted that the lack of a guard ring could be detected only at low Cs vapor pressures and high interelectrode voltage--i.e., low output voltages. The lack of a guard ring would, therefore, not affect the operation in the region of interest--namely, along the envelope of the J-V curves. In order to test these assertions, several pairs of J-V curves were taken with the guard ring of this converter and disconnected--i.e., floating electrically. Figure 3 shows three pairs of these J-V curves.

The solid lines were taken first with the guard floating; then the guard was connected and within ten seconds the dashed J-V curves were taken. The dashed curves are at slightly lower output potentials because the increased current to the guard cools the emitter and this is reflected in a reduction in output voltage. At the lowest Cs pressure and at low output voltage, there is a significant increase in the collector current density when the guard is floating. However, as predicted (7) this makes no significant difference at the knee of the J-V curve where it is tangent to the envelope of the J-V curves.

The guard tends to float at about 1.8 volts negative relative to the emitter. At zero output voltage (emitter to collector), since $\phi_{\rm C} = \phi_{\rm G}$, the surface of the guard is 1.8 volts negative relative to the surface of the collector. This potential difference between the guard and collector drives some electrons to the collector that normally would be collected at the guard.

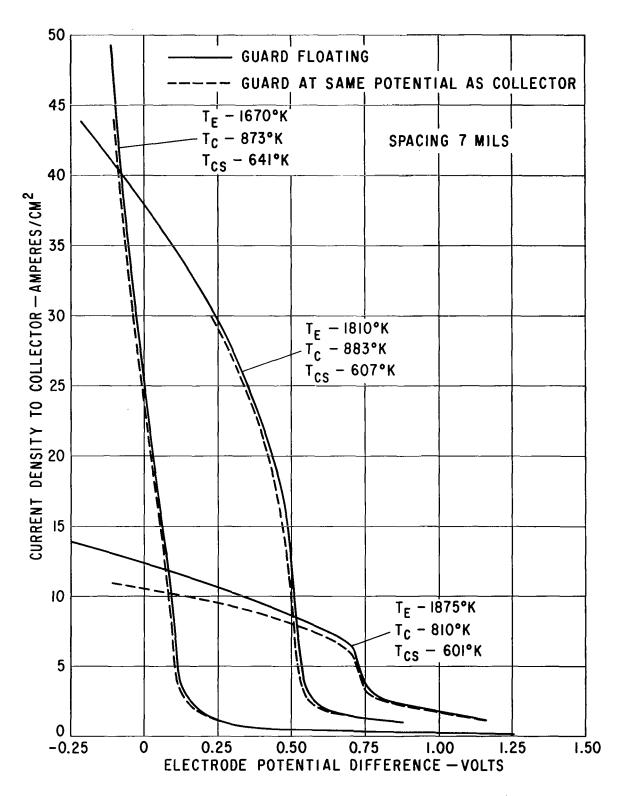


Figure 3. Change in J-V Curves Caused by Disconnecting the Guard

Following the above mentioned test of the effect of the guard, a set of J-V curves was run at $T_E = 1673^{\rm o}{\rm K}$, $T_C = 873^{\rm o}{\rm K}$, various Cs reservoir temperatures and at various spacings. When the emitter temperature was increased to $1770^{\rm o}{\rm K}$, the emitter supporting structure suddenly changed shape and tipped the emitter relative to the guard so that it was estimated that when the two electrodes touched on one side they were about 8 mils apart on the other side. The bell jar was removed to relevel the converter. Apparently a fourth leak had developed and the converter was exposed to an environment of air.

The converter was rebuilt and outgassed once more. In response to scheduling conflicts, the converter was cooled down and left for 10 days with an atmosphere of air on the outside and the inside connected to a vac-ion pump. The inside pressure was initially at 1×10^{-8} torr as measured in the ion pump. At the end of the 10-day period, the pressure had increased to 2×10^{-8} torr. By blowing Ar gas on local areas, a small leak was located in one of the 5-mil-thick Ni diaphragms. Argon gas does not pump well in an ion pump and the pressure will increase if Ar is admitted. When this leak was painted with G-Vac, the inside pressure returned to 1 x 10⁻⁸ torr. Because of this converter's historical record, it was decided to charge the device with Cs and mount the converter in the vacuum bell jar--trying to get the full set of data without reopening the bell jar. Once the converter was heated, it was believed that the G-Vac would be eventually evaporated off; however, it was hoped that the Cs would be lost very slowly. These problems are mentioned because they are important in making a plausible explanation for the observations to follow.

Figure 4 shows a J-V curve taken on June 7, 1968, and the first J-V run on August 27, 1968, after the treatment explained above. From 5 to 15 amperes/cm² the two J-V curves are very

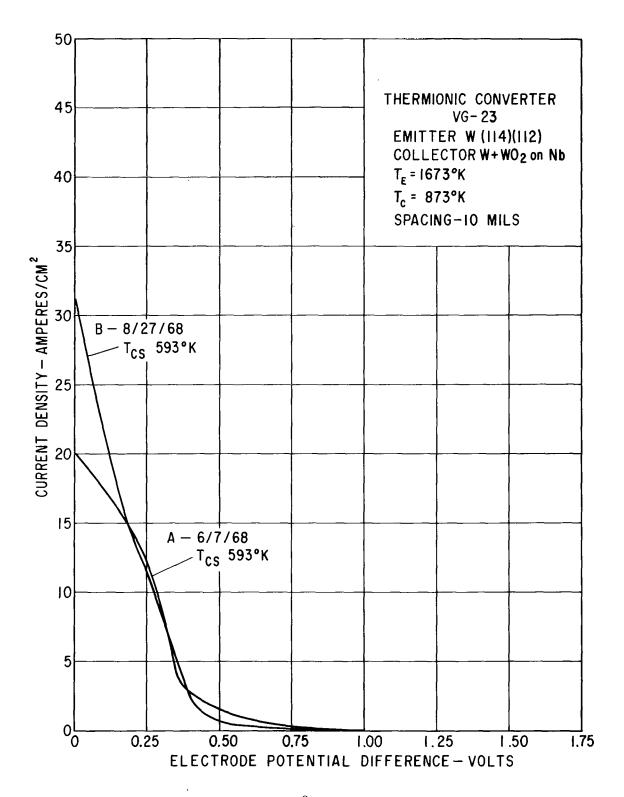


Figure 4. Performance at $T_{\rm E}$ = 1673 $^{\rm O}$ K Before and After Repairing an Envelope Leak

similar. This observation suggested that the work function of the converter drew 50% more current at zero output voltage. This observation would suggest that the emitter had a lower work function on August 27, 1968. On August 27 and 28, the converter was operated for about ten hours at T_E = 1770, 1865, and 1962°K. On August 29, a family of curves were taken at T_E = 1673°K. Curves D and E of Figure 5 are two of these curves. Curve C, taken on June 7, is shown for comparison.

Comparing Curve D with Curve C of Figure 5 and with Curve B of Figure 4, it appears that during the 10 hours of operation, the output voltage increased 0.1 volts, suggesting that the work function of the collector decreased 0.1 eV. However, Curve C was at $T_{Cs} = 603^{\rm O}{\rm K}$ and Curve D was at $T_{Cs} = 573^{\rm O}{\rm K}$. Therefore, one may conclude that the surface of the emitter also changed. Curve D has the same electron emission as Curve C, but for Curve D the Cs reservoir temperature is $30^{\rm O}{\rm K}$ lower.

A complete set of J-V curves was run up to and including $T_E = 2153^{\circ} K$ and a week later on September 5, 1968, another set of J-V curves was taken at $T_E = 1673^{\circ} K$. Curves E and F of Figure 5 were taken under identical conditions of T_E , T_{Cs} , and spacing. Apparently the electron emission of the emitter had improved still more.

Another complete set of data were run from September 5 through September 12, 1968. Comparing these J-V curves at the higher emitter temperature with those run August 29 and 30, it appears that the emitter changes were not detectable after August 29. However, the collector may have been decreasing its work function slightly; or, possibly the second complete set of data was taken at more nearly optimum collector temperatures. The data shown in Appendix A, Figures A-1 through A-36, are the last set of data taken from September 5 through 12, 1968.

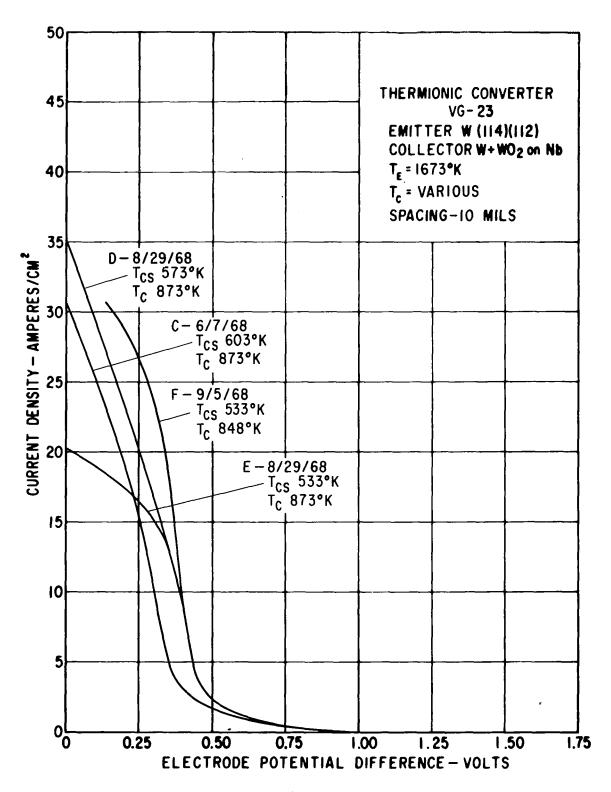


Figure 5. J-V Curves at $T_E = 1673^{\circ} K$ Showing Changes in Output Performance with Time

When the collector temperature was varied to select an optimum collector temperature, the results were at first puzzling. Figures 6 and 7 illustrate the problem. Reducing the collector temperature reduces the current density at V = O. After several runs, summarized at 10 amperes/cm² in Figure 8, it was finally concluded that the lower nickel foil had buckled and was touching a cool place on the thermal choke to the guard ring. This caused a secondary Cs reservoir to be formed at a temperature lower than the regular Cs reservoir temperature when the collector and guard were cooled. Therefore, the curves in Figures 6 and 7 were not taken at constant Cs vapor pressure; as T_C decreased, the effective T_{Cs} also decreased. Recognizing this difficulty, the curves at $T_E = 1957$ and 2057^{O} K in Figure 8 were not carried to low T_C values.

A review was made of all the curves presented in the Appendix. In those cases where it was thought probable that a second reservoir had formed, the T_{Cs} value was preceded by a < sign.

The families of curves in Figures 9 and 10 show less output voltage at the greater current densities than for other converters tested in this program. These curves are envelopes of families of J-V curves at various Cs pressures. Because of the second reservoir, high Cs pressures necessary to draw large currents were not obtained. This probably explains the lower output voltages at high current densitites. Another possibility is that a coating of W + WO₂ on the collector and described in the next section had sufficient resistance to reduce the output voltage at high current densities.

Toward the end of testing this converter, intermittent short circuits between the emitter and guard developed at spacings of 2 to 5 mils. The cause of these will be explained in the next section.

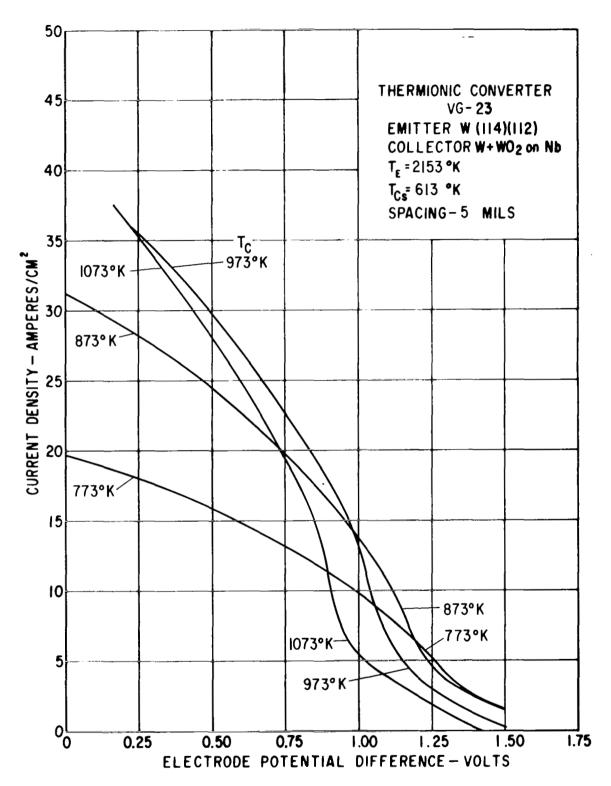


Figure 6. J-V Curves at T = 2153 $^{\rm O}$ K, T $_{\rm Cs}$ = 613 $^{\rm O}$ K and 5-mil Spacing for Various Collector Temperatures

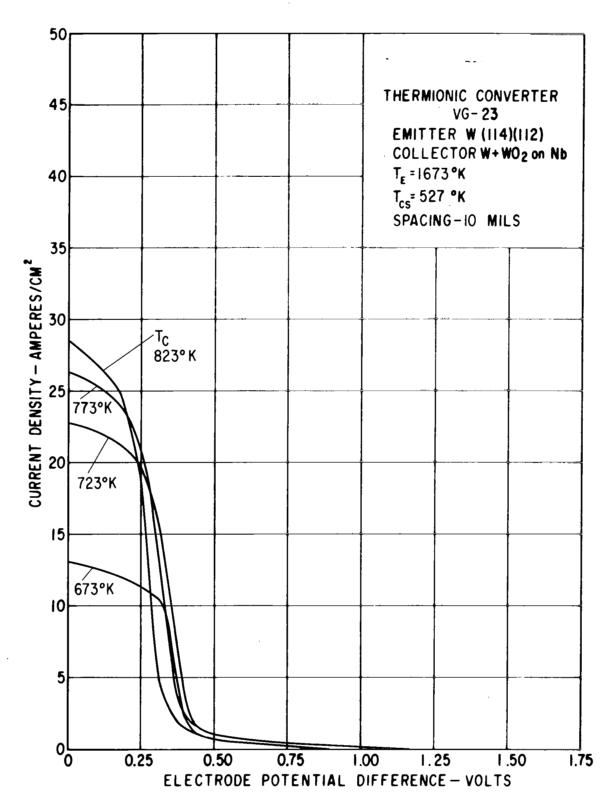


Figure 7. J-V Curves at T_E = 1673 $^{\rm o}$ K, $T_{\rm Cs}$ = 527 $^{\rm o}$ K and 10-mil Spacing for Various Collector Temperatures

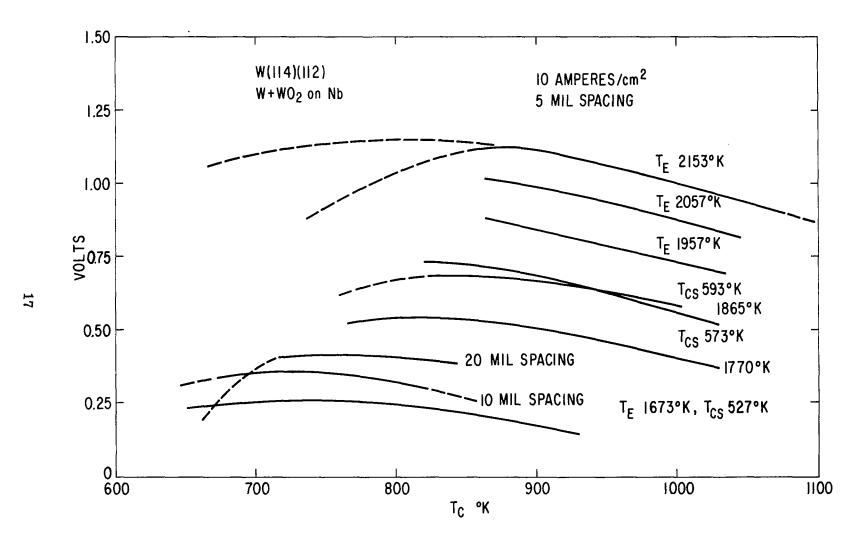


Figure 8. A Summary of the Output Potential Versus Collector Temperature for Several Emitter Temperatures all at 10 Amperes/cm² and 5-mil Spacing (Except as Noted)

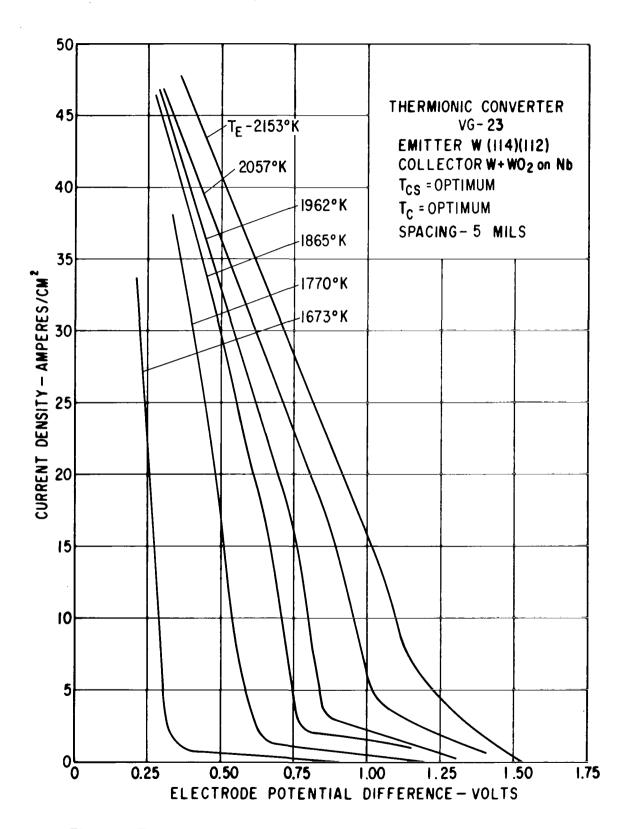


Figure 9. Envelopes of J-V Curves at Various Emitter Temperatures; 5-mil Spacing $\rm T_{Cs}$ and $\rm T_{c}$ Optimized.

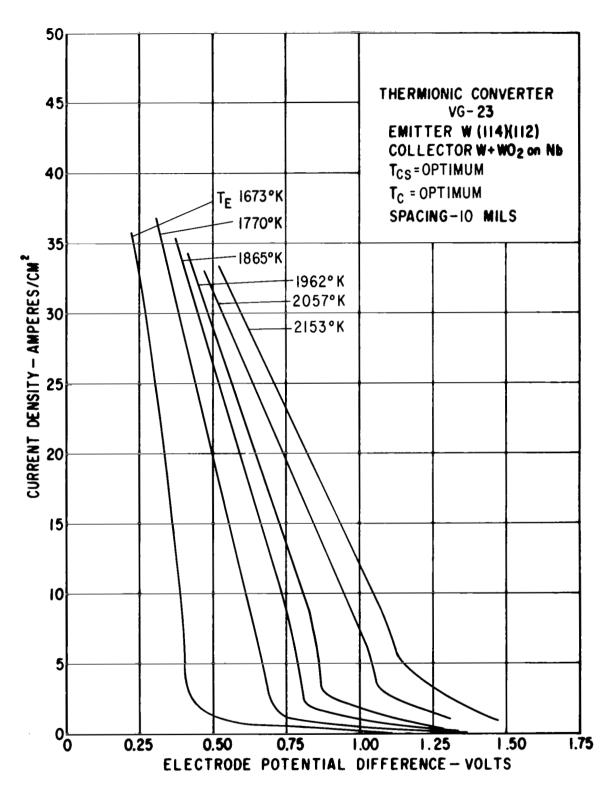


Figure 10. Envelopes of J-V Curves for Various Emitter Temperatures;10-mil Spacing, $\rm T_{C}$ and $\rm T_{Cs}$ Optimized

CHARACTERIZATION OF THE ELECTRODES AFTER CONVERTER OPERATION

Figure 11 shows the appearance of the collector and guard after operation. Both electrodes were coated with a dark grey deposit. On some areas of the guard, the deposit looked like a black powder, but at a magnification of 640 or more the darkest areas appeared like a forest of dendrites. Figure 12 shows the emitter. Some of the black material from the guard is apparent on the outer part of the emitter. This material probably got onto the emitter after testing and while handling the converter to open it. Apparently this deposit caused the intermittent short circuits observed toward the end of testing.

Light scrapings were taken of the deposit at the center of the collector and examined by x-ray diffraction. All the diffraction lines were accounted for by the presence of elemental W and WO₂. No Nb or niobium oxides were observed.

The emitter appeared to be clean except where the deposit from the guard adhered. Large grains were easily discernible with the naked eye. One grain near the center was 1/4-inch long. An x-ray diffraction analysis showed that this was oriented with the (112) planes very nearly parallel to the surface. The entire surface of the emitter, when observed at a 240X magnification, showed small cavities with planar bottoms (see Figure 13). These cavities or pits were most numerous on the large (112) oriented grain. Three other grains were examined by x-ray diffraction and visually in the microscope. One grain had (114) orientation and the other two were of a (113) orientation. The bottom of the pits on these grains were tipped the correct angle from the grain orientation to expose the (112) surfaces. Assuming that all the planar areas at the base of the pits were (112) planes, a probable orientation of the entire emitter could

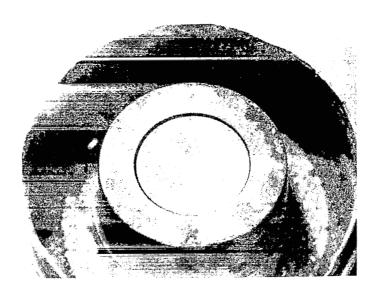


Figure 11. Photograph of the Collector After Converter Operation

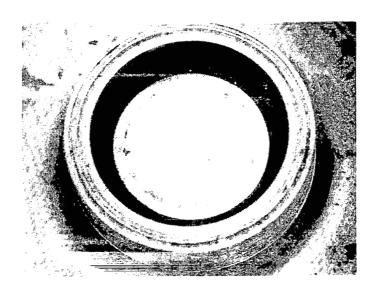


Figure 12. Photograph of the Emitter After Converter Operation



Figure 13. Microphotograph of the Emitter, $240\mathrm{X}$.

be inferred. Figure 14 shows a map of these observations. The grains that were checked by x-ray diffraction have the orientation underlined. The orientation of the other grains was by visual observation of the slopes of the flat areas, assuming these flats were (112). Regions marked f. g. were fine grain regions. No (100) oriented grains were observed.

This emitter was originally (100) oriented. It has been demonstrated that in a good vacuum, W foils tend to undergo secondary recrystallization with the (110) planes exposed.* However, Walter and Dunn (11) have demonstrated that for many metals the presence of slight contamination of H_2O vapor or O_2 alters the surface energies so that other directions are preferred during secondary recrystallization. For example, body center cubic 3% silicon iron grows (110) crystallites in vacuum and (100) in the presence of O_2 . The growth in O_2 of (112) planes has never been observed. Mr. John Walter, who has been studying the recrystallization of W wires and sheets, believes that O2 gas or O2 from the dissociation of H2O on the emitter surface would tend to favor the (100) orientation in secondary recrystallization of a body centered cubic material such as W. Also, the surface-to-volume ratio of the 20-mil layer is probably not sufficiently great for the surface energy to provide the driving force for secondary recrystallization. Therefore, he is of the opinion that the O_2 present did not cause the orientation to be changed to (112); rather, in the first few layers of the vapor deposited W there were many crystallites of (112), (113), and (114) orientation which during the high temperature treatments grew at the expense of the (100) columnar grains until the (112) to (114) orientation reached the surface.

^{*}Personal communication with J. L Walter.

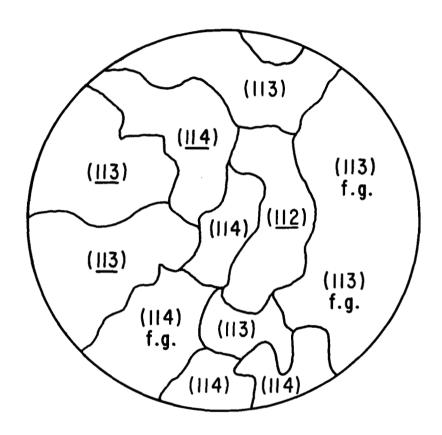


Figure 14. Map of the Emitter after Converter Operation. Underlined Orientations were Checked by X-ray Diffraction. Other Areas Inferred Assuming Bottom of Pits were 112 surfaces. (f. g. means fine grain area)

L. H. Germer and J. W. May, ⁽¹²⁾ in studying the effect of O₂ on a (110) face of W, reported, "The surface can always be freed from oxygen by flashing at 2000°K with no rise in pressure, which probably means that the oxygen is removed by the evaporation of oxides". N. J. Taylor ⁽¹³⁾ observed that O₂ facets a (111) face of W leaving the (112) planes exposed.

It is postulated that in this case, first the 20-mil layer underwent growth of (112), (113) and (114) crystallites at the expense of the (100) columnar grains. Subsequently the O_2 by the removal of WO_2 faceted the (113), (114) and (112) crystallites exposing the $\{112\}$ planes at the base of pits.

COMPARISON WITH OTHER CONVERTERS

Figure 15 compares the output power versus T_E for three converters at 10-mil spacing and 10 amperes/cm²; T_C and T_{Cs} are optimized. The output of this converter is less than the converter with W (100) {110} emitter and Nb collector. Except at the highest emitter temperature, this converter produces more output than the converter with a polycrystalline W emitter and a Nb collector.

One way to improve the output of a converter is to develop an emitter surface that, at a particular temperature, produces high electron emission at relatively low Cs pressure. The lower Cs reduces the electron scattering in the plasma and reduces the plasma losses; accordingly, the lower Cs pressure permits one to operate the converter at a wider spacing. Figure 16 compares a J-V curve from this converter with curves from two other converters at $T_{E} = 2153^{\circ}$ K. The emitter of this converter produces higher current densities at lower Cs pressures than any other converter tested in this program. Notice that at $T_F = 2153^{\circ}K$ and $T_{Cs} = 603^{\circ}K$, the current density at electrode voltages of 1 volt or less is greater than for the W (110) {110} at 10°K higher Cs reservoir temperature. The high emission of this emitter is even more pronounced at low emitter temperatures as demonstrated in Curves A, B and C of Figure 17. Curve D of Figure 17 is a J-V trace for the lowest T_{Cs} reservoir temperature observed in this program for a converter generated power in the discharge mode.

According to the excellent work by Coggins and Stickney, (14) W(110) should give higher electron emission in Cs vapor than W(112). In field emission studies, Houston observed that the (116) planes of W have a low work function in vacuum. The W atoms on the (116), (114), and (113) planes are loosely packed. One would expect that, in the presence of Cs, all of these orientations would give less

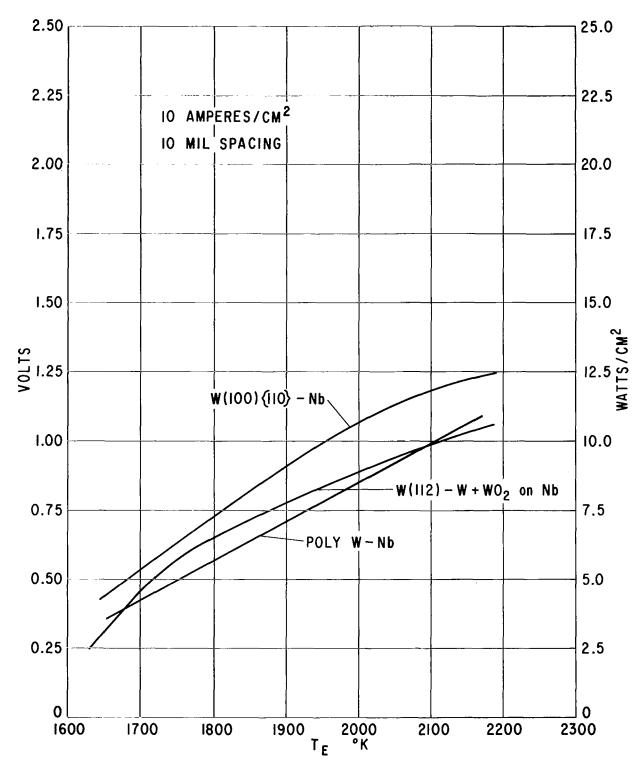


Figure 15. Comparison of Output Performance of Three Converters at 10 Amperes/cm² and 10-mil Spacing. (In the hyphenated pairs, the emitter surface is indicated before the hyphen and the collector after the hyphen.)

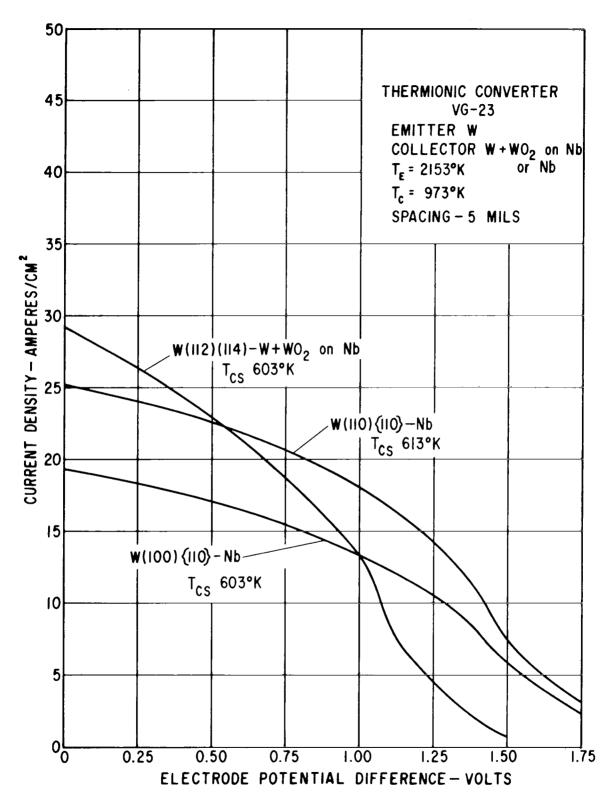


Figure 16. J-V Curves for the Three Converters of Figure 15 Under Similar Conditions at $T_{\rm E}$ = 2153 $^{\rm O}$ K.

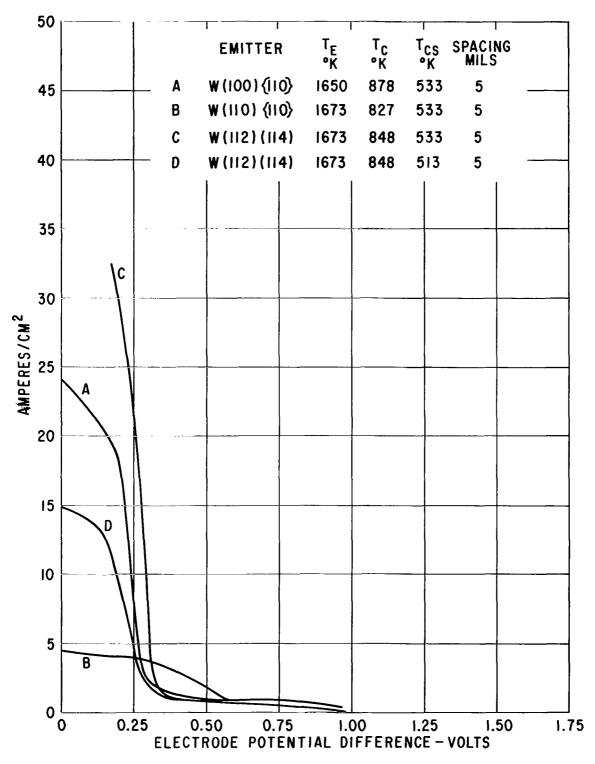


Figure 17. J-V Curves for the Three Converters of Figure 15 at T_E = 1673° K-Notice the low T_{Cs} Value for Curve D.

emission than the (100) planes and much less than the (110) planes. The presence of O_2 in this converter may be responsible for this high electron emission from the cesiated surface.

Returning to Figure 16, it is apparent that this converter produces lower voltage at current densities of 15 amperes/cm² or less. Part of this effect is caused by the fact that the collector was hotter than the optimum temperature (see Figure 8). The work function of the collector and the end of testing showed a minimum value of 1.44 eV. This low value probably is the result of the W + WO₂ on the Nb. An unexplained anamoly exists--namely, with this low collector work function, why is the output voltage of this converter as much as 0.3 volt lower than the other two converters?

DISCUSSION

It is well known that extremely small amounts of H₂O vapor in a W filament lamp will shorten the life of the lamp by depositing much more W on the glass bulb than would be transferred by evaporation. The so-called "water cycle" is as follows. On the hot W surface:

$$2H_2O \rightarrow 2H_2 + O_2$$

$$W + O_2 \longrightarrow WO_2$$

The WO_2 is volatile at the filament temperature and deposits on the glass. At the glass temperature, H_2 reduces WO_2 to produce $W + 2H_2O$ The two H_2O molecules go back to the filament to bring back another W atom. By this regenerative process, a small amount of H_2O can transport a large amount of W.

In the presence of Cs vapor, the reaction is probably much more complicated. Perhaps Cs_2O forms a cycle like the H_2O cycle and H_2O vapor is not involved. In this experiment, if the reaction had been a simple H_2O cycle, the deposit on the collector and guard would have been pure W. From the x-ray diffraction line intensities of the material on the collector, one would conclude that there was more than a trace of WO_2 ; rather, about 40% of the deposit may have been WO_2 .

The coating on the guard, collector and also on a Ni foil in an area that could "see" the emitter was about 0.5-micron thick with crystalline dendrites extending 6 to 9 microns. The total area covered was about 8 cm². It is hard to estimate the volume or

density of this material. However, a rough estimate indicates that if 40% of the volume of the material was WO_2 , it would have required 0.9 x 10^{-5} moles of O_2 . This would be 2 x 10^{-2} cc of O_2 at standard temperature and pressure.

The inside of the converter has a volume of about 60 cc; therefore, this amount of O_2 would be about 0.25 torr. At the time the converter was sealed from the pump, the pressure was 10^{-8} torr. Where did all the O_2 come from? If it was adsorbed on the inside surfaces of the converter, it would have been 12 molecular layers deep. This seems improbable; however, J. R. Young* has recently measured 4 molecular layers on Be and 39 molecular layers of O_2 on Ti, so possibly the Mo, Ni, Nb and Al_2O_3 surfaces held the O_2 as an oxide layer at room temperature and gave it up at the operating temperatures. It has been reported that under some conditions the output performance of a thermionic converter may be enhanced by admitting O_2 between the collector and the emitter. (8, 15) This experiment suggests that the introduction of O_2 must be carefully controlled to avoid transport of emitter material to the collector.

^{*}Private communication with J. R. Young.

CONCLUSIONS

This converter was initially fabricated with a (100) oriented W emitter and a Nb collector. During operation, the crystal structure of the emitter changed to a (112) to (114) orientation and W + WO_2 was deposited on the Nb collector. The performance data presented herein is, therefore, associated with the latter surface characteristics.

The presence of the deposit on the collector emphasizes the importance of the outgassing procedure in building converters.

The grain growth in the emitter probably was not caused by the presence of O_2 . However, the performance of the emitter appeared to be enhanced by the O_2 .

SYMBOLS AND DEFINITIONS

Sumbala	Definitions
Symbols	Delititions
ϕ	Work function - electron volts
$\phi_{ m E}$	Work function of emitter
$\phi_{ m C}$	Work function of collector
eV	Electron volts
$^{ extsf{T}}_{ extsf{E}}$	Temperature of emitter
^T C	Temperature of collector
$^{\mathrm{T}}$ Cs	Temperature of cesium reservoir
J-V	Current density versus voltage curves
$\phi_{ m G}$	Work function of guard

REFERENCES

- (1) Wilson, V. C. and Lawrence, J., Adv. Energy Conv. <u>4</u>, 195 (1964).
- (2) Wilson, V. C., Therm. Conv. Spec. Conf., p. 285 (1964).
- (3) Lawrence, J., Therm. Conv. Spec. Conf., p. 291 (1964).
- (4) Wilson, V. C., Webster, H. F., and Lawrence J., International Therm. Power Conf., London, England, Sec. IIIA (1965).
- (5) Lawrence, J. and Perdew, J. P., Therm. Conv. Spec. Conf., p. 289 (1965).
- (6) Lawrence, J. and Wilson, V. C., Therm. Conv. Spec. Conf., p. 6 (1966).
- (7) Wilson, V. C. and Lawrence, J., "Characteristics of a Variable Space Planar Thermionic Converter with a Tungsten Emitter and a Niobium Collector," NASA CR-1033, 1968.
- (8) Wilson, V. C., and Lawrence, J., Therm. Conv. Spec. Conf. (1967), NASA CR-1381.
- (9) Wilson, V. C. and Podkulski, S. P., "Characteristics of a Thermionic Converter with a Chloride Vapor Deposited Tungsten Emitter (110) and a Nickel Collector," NASA CR-1416, 1969.
- (10) Festa, J. V. and Danko, J. C., Proc. of Conf. on Chem. Vapor Deposition of Refractory Metals, Alloys and Compounds, Gatlinburg, Tenn., September (1967).
- (11) Walter, J. L. and Dunn, C. G., Acta Met. 8, 497 (1960).
- (12) Germer, L. H. and May, J. W., Surf. Sci. 4, 452 (1966).
- (13) Taylor, N. J., Surf. Sci. <u>2</u>, 544 (1964).
- (14) Coggins, J. L. and Stickney, R. E., Surf. Sci. 11, 355 (1968).
- (15) Levine, J. D., Harbaugh, W. E., and Shoemaker, R. E., Proc. Therm. Conv. Spec. Conf., p. 276 (1965); Lieb, D. and Kitrilakis, S. S., Proc. Therm. Conv. Spec. Conf., p. 348 (1966).

APPENDIX A

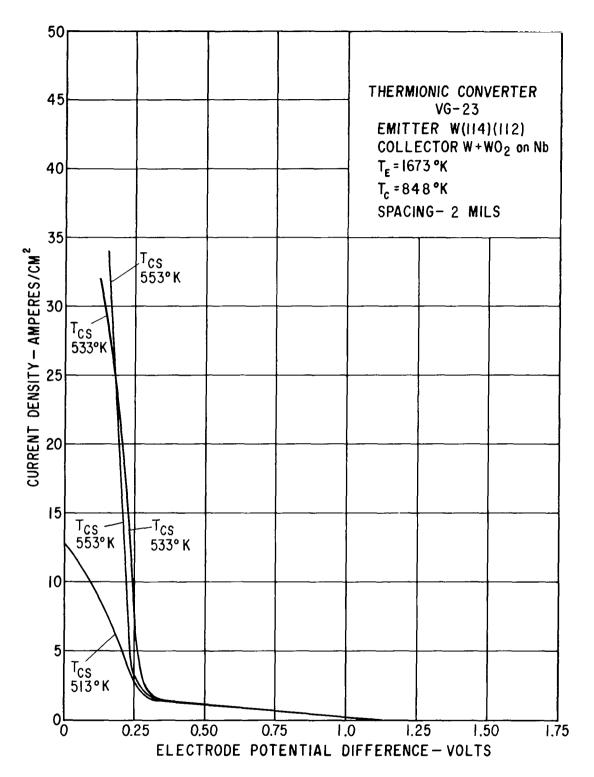
Output Characteristics of a Thermionic Converter with a W(112) to (114) Emitter and a Collector of W + WO $_2$ on Nb

The following data were taken after the converter appeared to become stable with time.

Figure	T _E (°K)	т _с (°К)	T _{Cs} (°K)	Spacing (mils)
18(a) 18(b) 18(c) 18(d) 18(e) 18(f)	1673 1673 1673 1673 1673	848 848 848 848 848	513 to 553 513 to 553 513 to 553 513 to 553 513 to 553 553	2 5 7 10 20 2 to 20
19(a) 19(b) 19(c) 19(d) 19(e) 19(f)	1770 1770 1770 1770 1773 1770	873 873 873 873 873 873	533 to 573 533 to 573 533 to 573 533 to 573 533 to 573 553	2 5 7 10 20 2 to 20
20(a) 20(b) 20(c) 20(d) 20(e) 20(f)	1865 1865 1865 1865 1865	923 923 923 923 923 923	553 to <593* 553 to <593 553 to <593 553 to <593 553 to <593 573	2 5 7 10 20 2 to 20
21(a) 21(b) 21(c) 21(d) 21(e) 21(f)	1962 1962 1962 1962 1962 1962	948 942 948 948 948 948	573 to <613 573 to <613 573 to <613 573 to <613 573 to <613 573	2 5 7 10 20 2 to 20
22(a) 22(b) 22(c) 22(d) 22(e) 22(f)	2057 2057 2057 2057 2057 2057	948 948 948 948 948	583 to <613 583 to <613 583 to <613 583 to <613 583 to <613 603	2 5 7 10 20 2 to 20

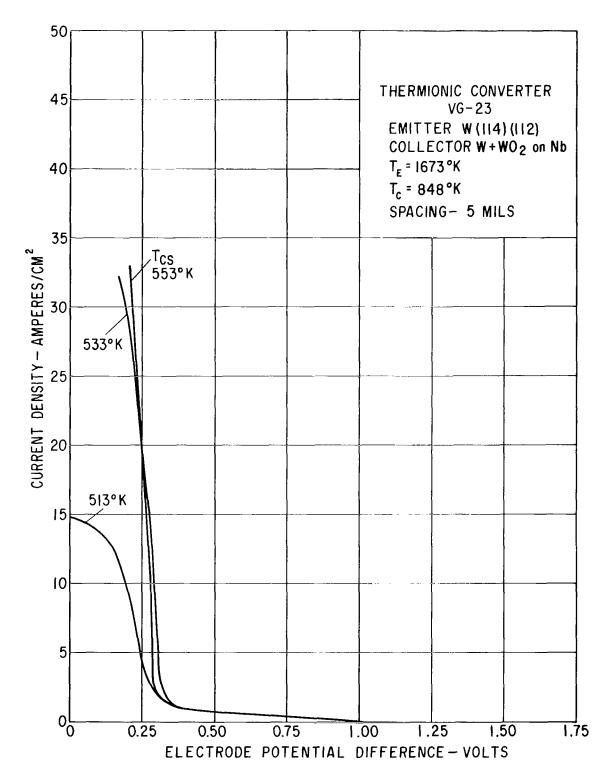
^{*}For explanation of < sign, see page 14.

Figure	T _E (°K)	T _c (°K)	T _{Cs} (°K)	Spacing (mils)
23(a)	2153	973	603 to <643	2
23 (b)	2153	973	603 to <643	5
23 (c)	2153	973	603 to <643	7
23 (a)	2153	973	603 to <643	10
23 (e)	2153	973	603 to <643	20
23 (f)	2 153	973	623	2 to 20



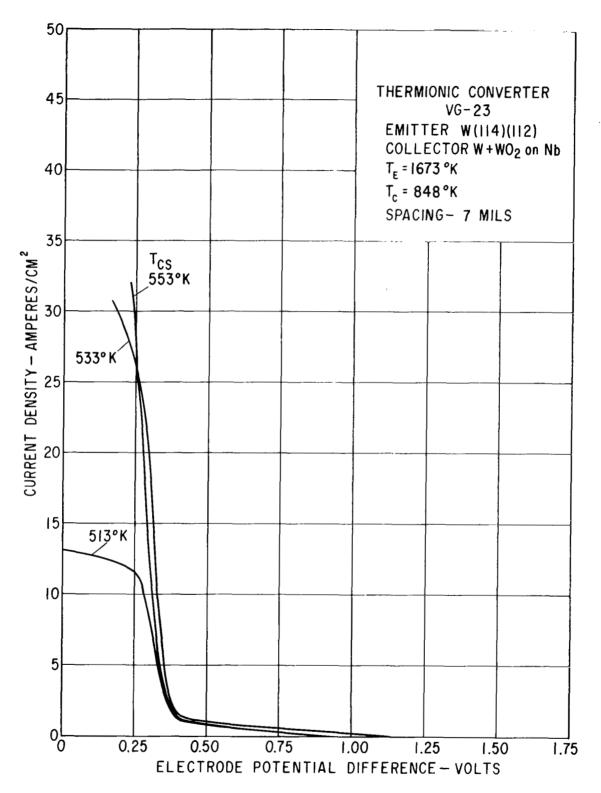
(a) Spacing, 2 mils; cesium temperature, $513^{\rm O}$ to $553^{\rm O}$ K.

Figure 18. - Output characteristics of thermionic converter with W(112) to (114) emitter and collector of W + WO $_2$ on Nb. Emitter temperature, 1673 $^{\rm O}$ K; collector temperature, 848 $^{\rm O}$ K.



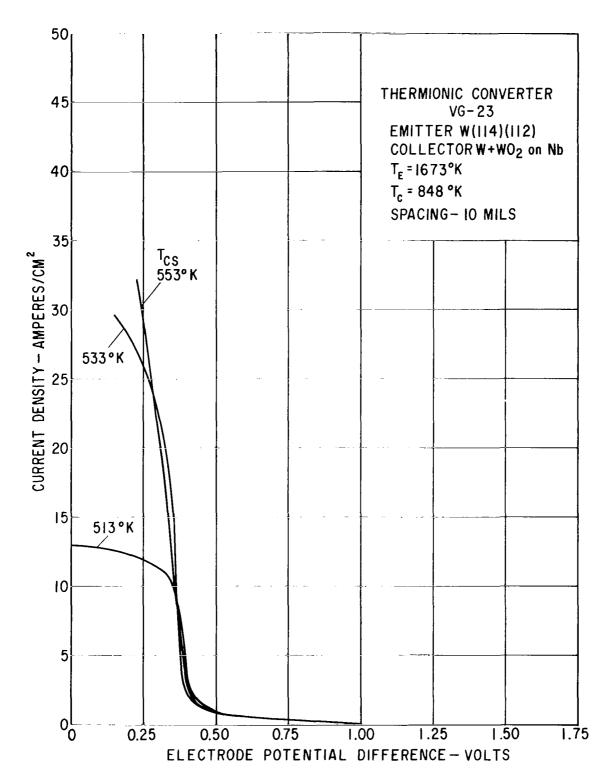
(b) Spacing, 5 mils; cesium temperature, 513° to 553° K.

Figure 18. - Continued.



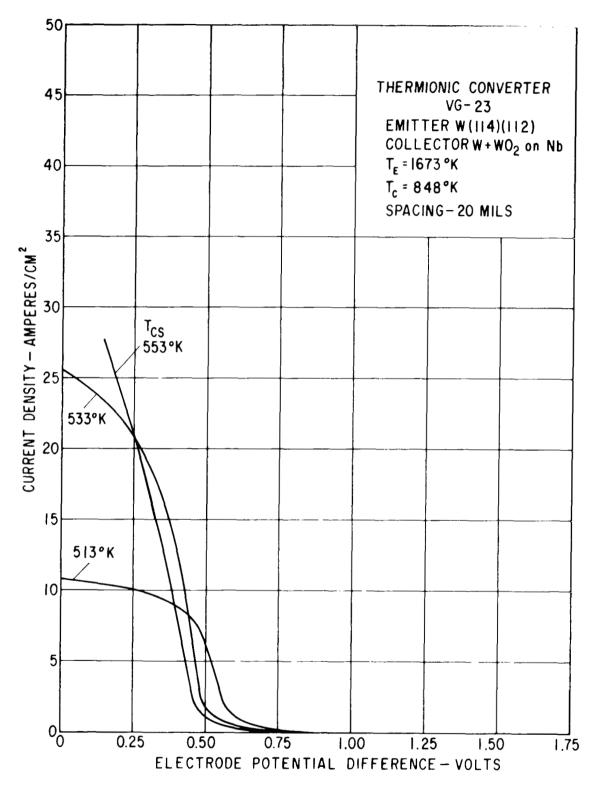
(c) Spacing, 7 mils; cesium temperature, 513° to 553° K.

Figure 18. - Continued.



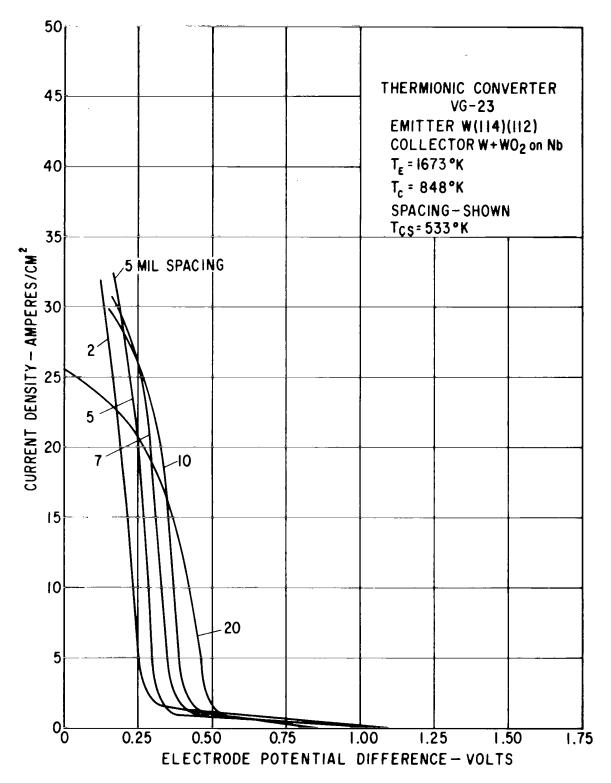
(d) Spacing, 10 mils; cesium temperature, $513^{\rm O}\,{\rm to}\,553^{\rm O}\,{\rm K}$.

Figure 18. - Continued.



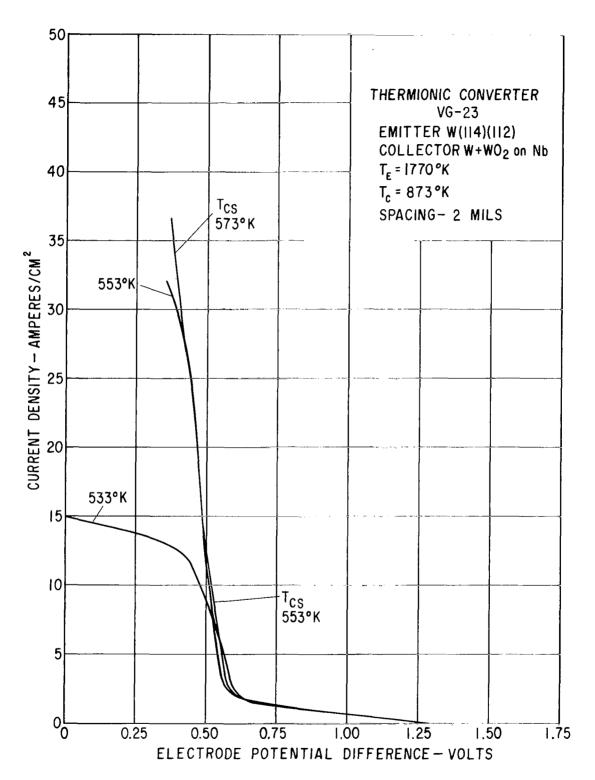
(e) Spacing, 20 mils; cesium temperature, $513^{\rm O}$ to $553^{\rm O}$ K.

Figure 18. - Continued.



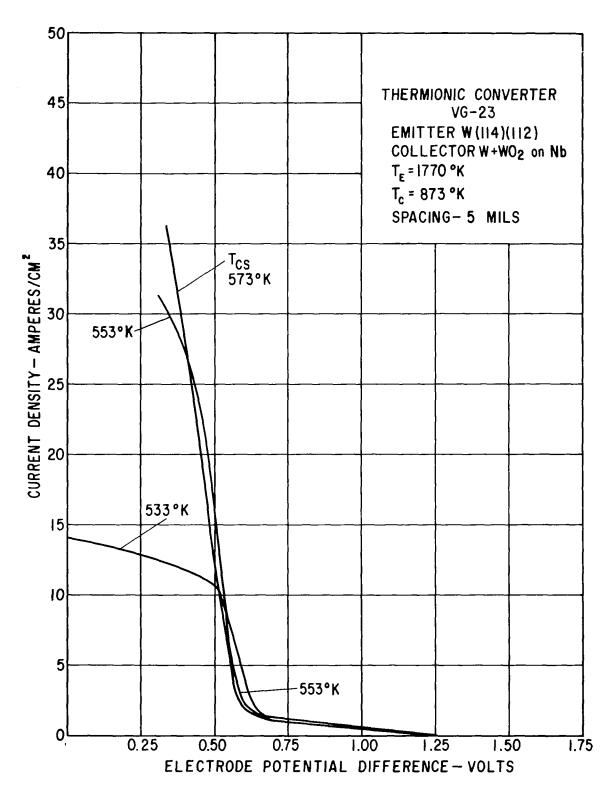
(f) Spacing, 2 to 20 mils; cesium temperature, 553° K.

Figure 18. - Concluded.



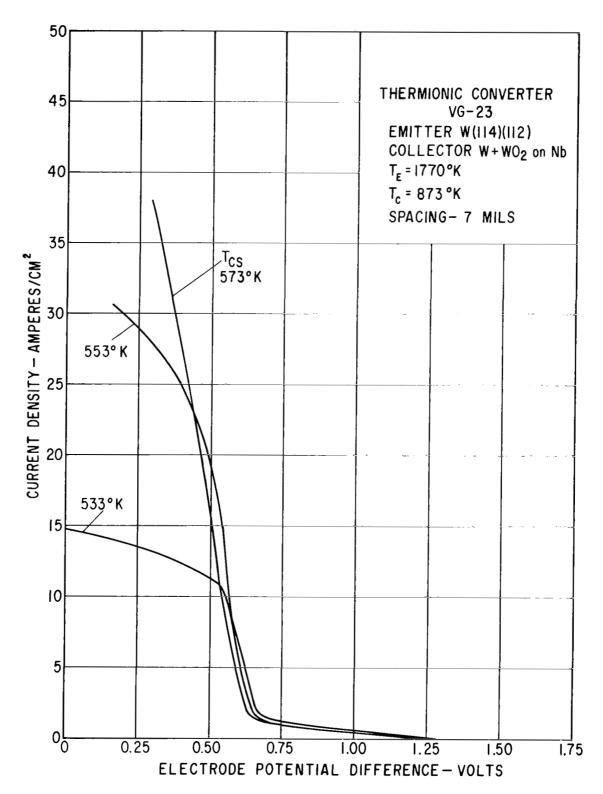
(a) Spacing, 2 mils; cesium temperature, 533° to 573° K.

Figure 19. - Output characteristics of thermionic converter with W(112) to (114) emitter and collector of W + WO $_2$ on Nb. Emitter temperature, 1770 $^{\rm O}$ K; collector temperature, 873 $^{\rm O}$ K.



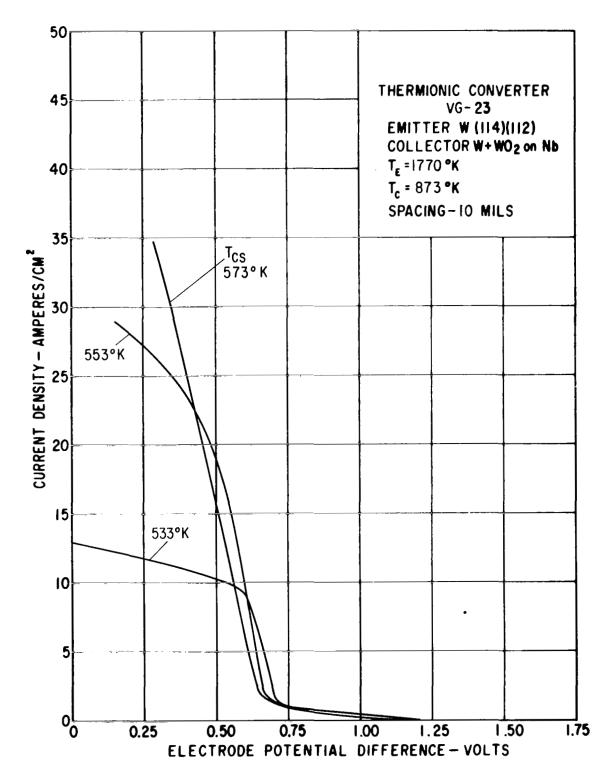
(b) Spacing, 5 mils; cesium temperature, $533^{\rm O}$ to $573^{\rm O}$ K.

Figure 19. - Continued.



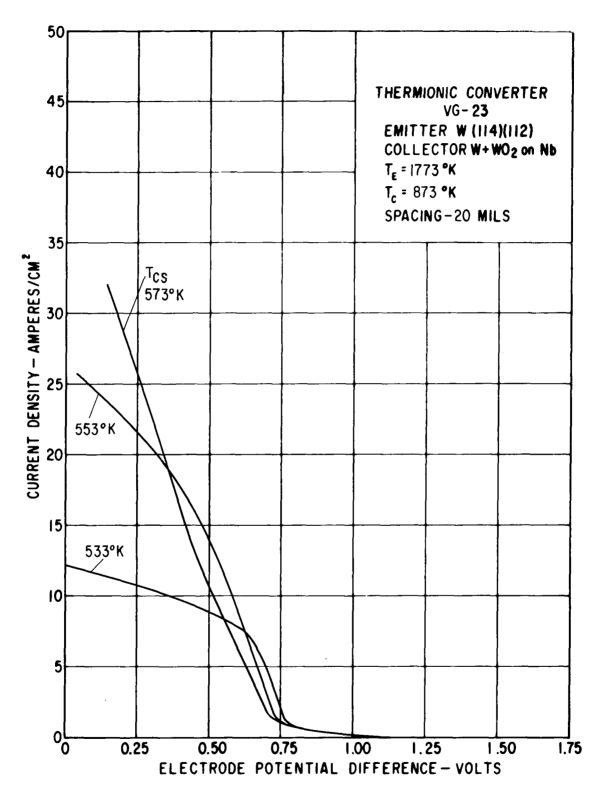
(c) Spacing, 7 mils; cesium temperature, 533° to 573° K.

Figure 19. - Continued.



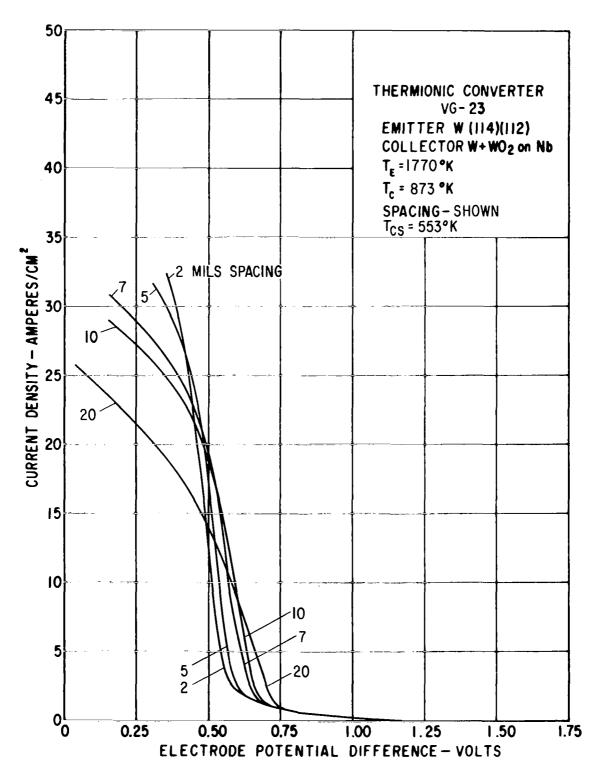
(d) Spacing, 10 mils; cesium temperature, $533^{\rm O}$ to $573^{\rm O}$ K.

Figure 19. - Continued.



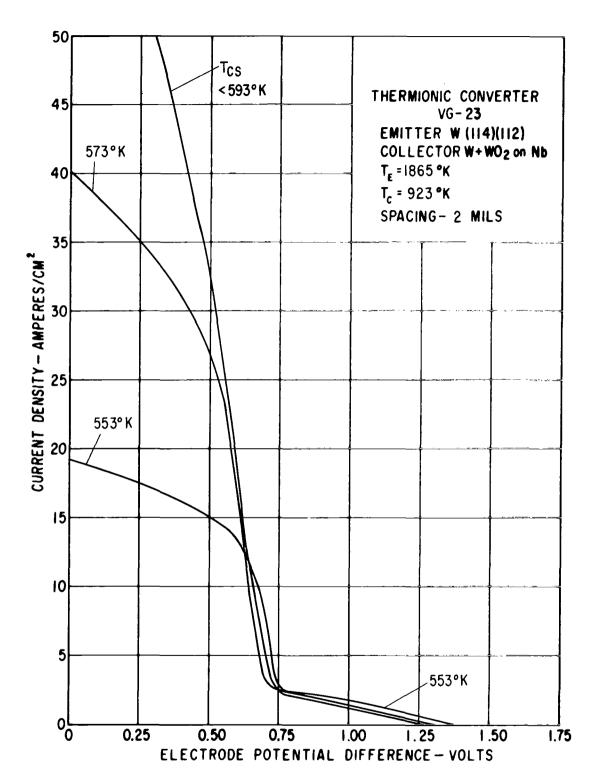
(e) Spacing, 20 mils; cesium temperature, $533^{\rm O}$ to $573^{\rm O}$ K.

Figure 19. - Continued.



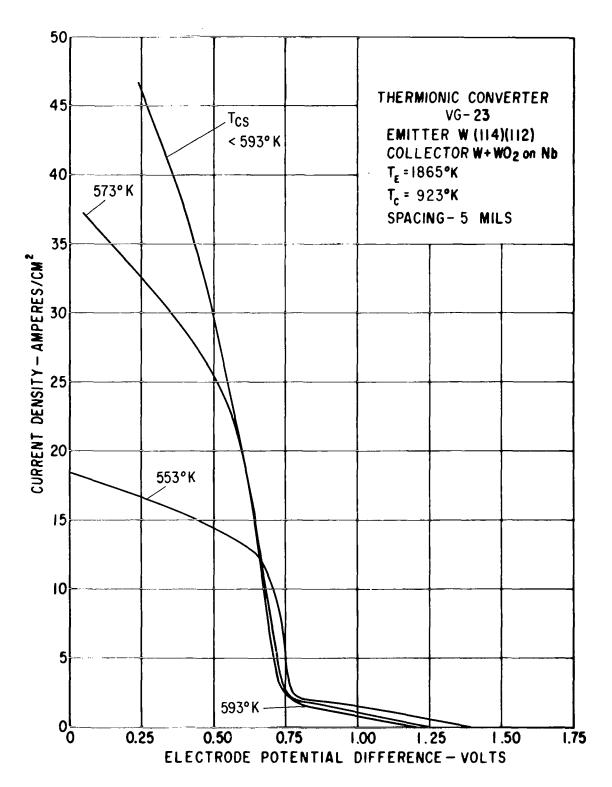
(f) Spacing, 2 to 20 mils; cesium temperature, $553^{\rm O}$ K.

Figure 19. - Concluded.



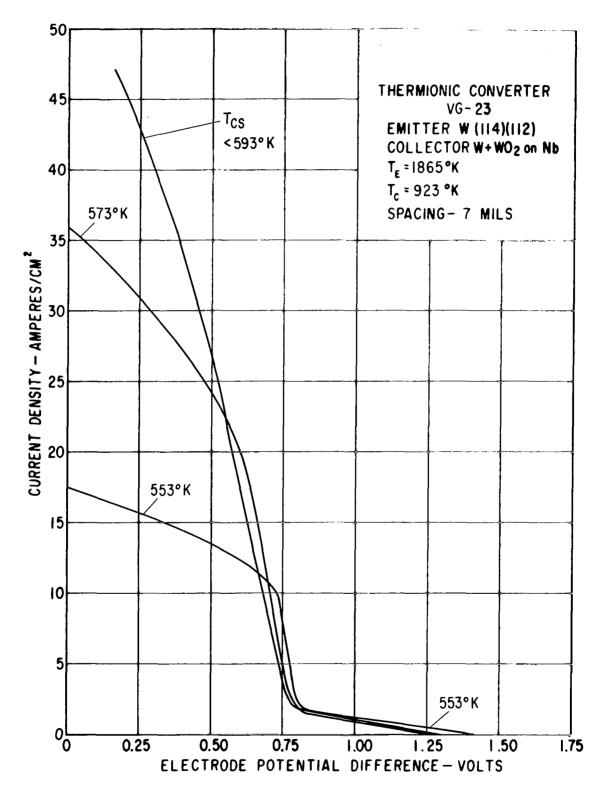
(a) Spacing, 2 mils; cesium temperature, $553^{\rm O}\,{\rm to}\,{<}593^{\rm O}\,{\rm K}.$

Figure 20. - Output characteristics of thermionic converter with W(112) to (114) emitter and collector of W + WO $_2$ on Nb. Emitter temperature, 1865 $^{\rm O}$ K; collector temperature, 923 $^{\rm O}$ K.



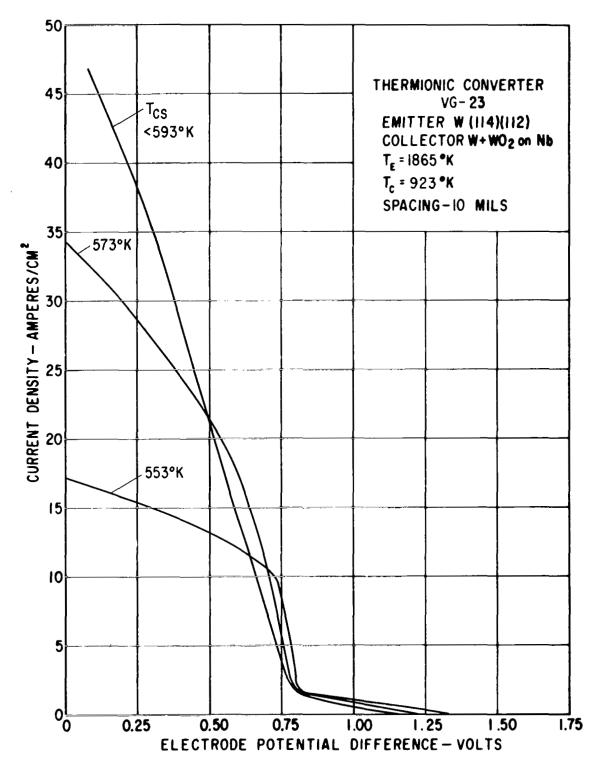
(b) Spacing, 5 mils; cesium temperature, $553^{\rm O}$ to ${<}593^{\rm O}$ K.

Figure 20. - Continued.



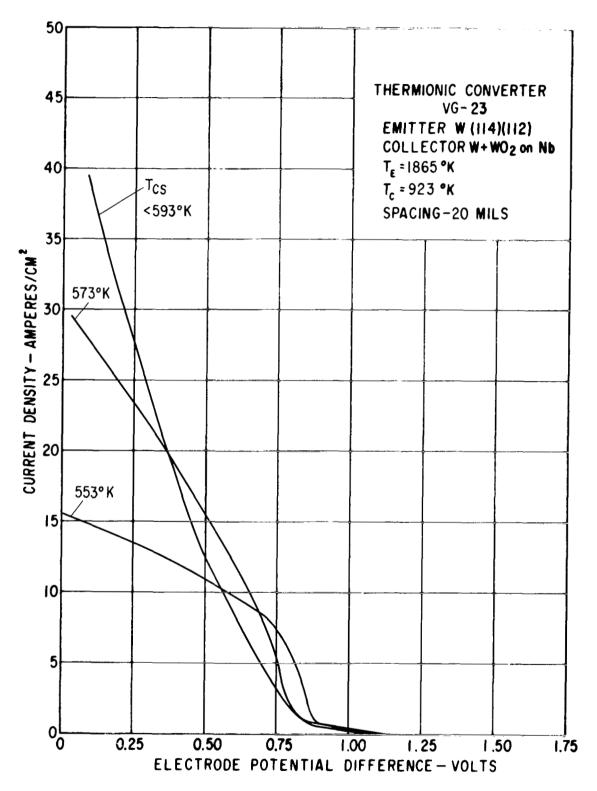
(c) Spacing, 7 mils; cesium temperature, 553° to $<593^{\circ}$ K.

Figure 20. - Continued.



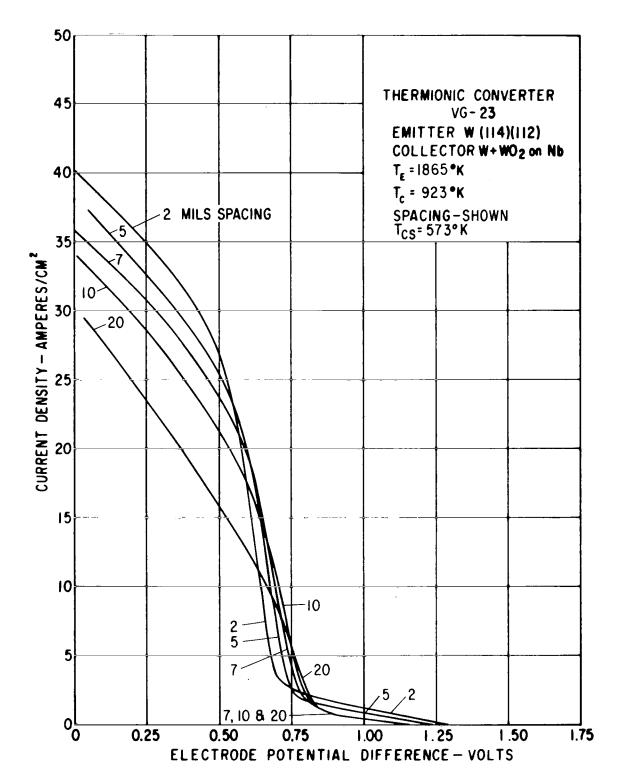
(d) Spacing, 10 mils; cesium temperature, $553^{\rm O}$ to ${<}593^{\rm O}$ K.

Figure 20. - Continued.



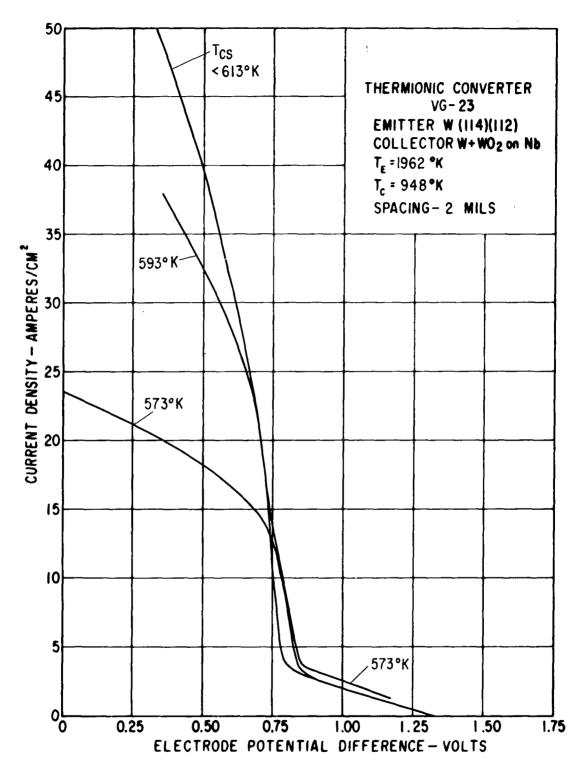
(e) Spacing, 20 mils; cesium temperature, 553° to <593° K.

Figure 20. - Continued.



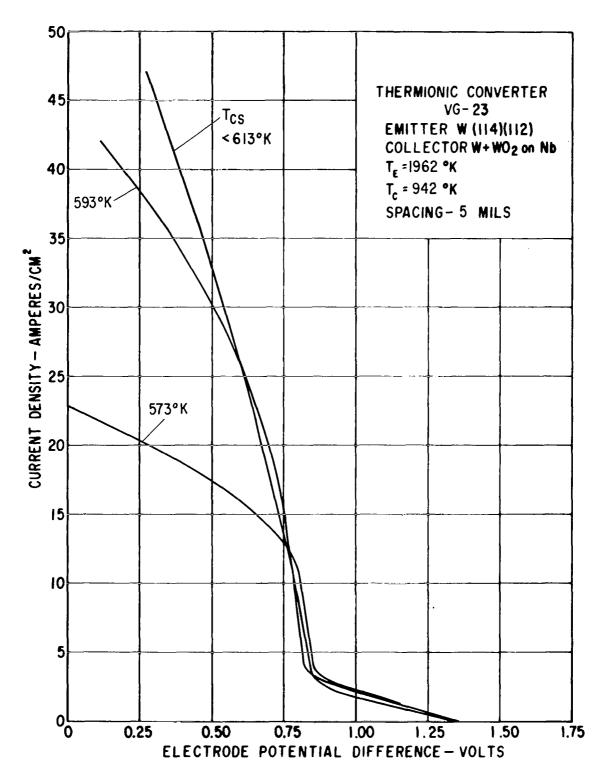
(f) Spacing, 2 to 20 mils; cesium temperature, $573^{\mbox{\scriptsize O}}$ K.

Figure 20. - Concluded.



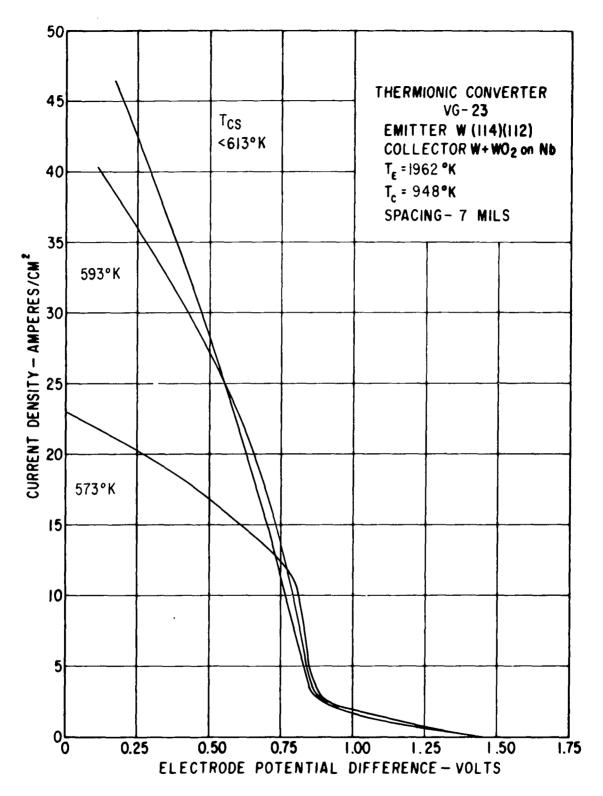
(a) Spacing, 2 mils; cesium temperature, 573° to <613° K.

Figure 21. - Output characteristics of thermionic converter with W(112) to (114) emitter and collector of W + WO $_2$ on Nb. Emitter temperature, 1962 $^{\rm O}$ K; collector temperature, 948 $^{\rm O}$ K.



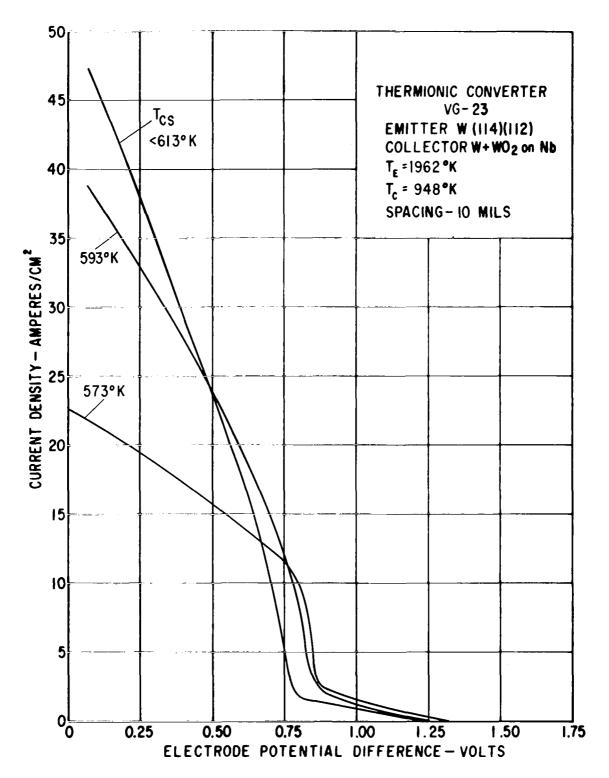
(b) Spacing, 5 mils; cesium temperature, 573° to $<613^{\circ}$ K.

Figure 21. - Continued.



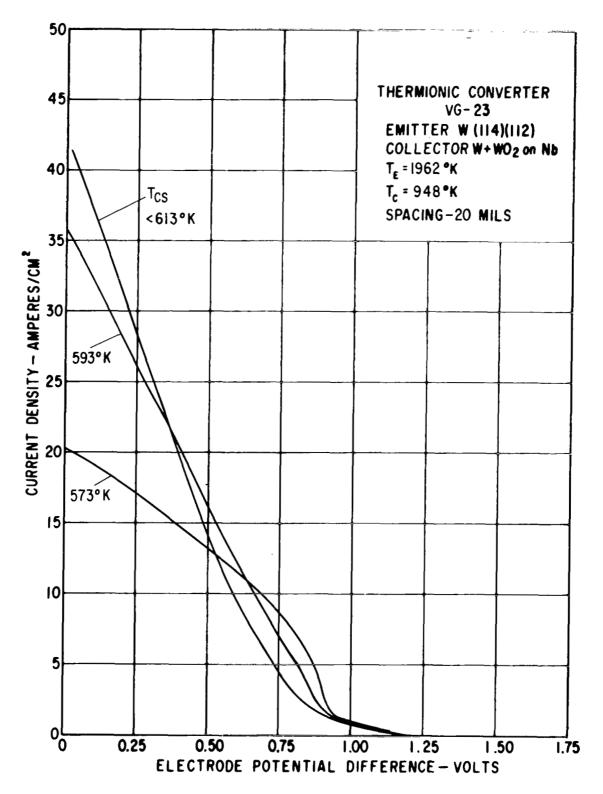
(c) Spacing, 7 mils; cesium temperature, 573° to $<613^{\circ}$ K.

Figure 21. - Continued.



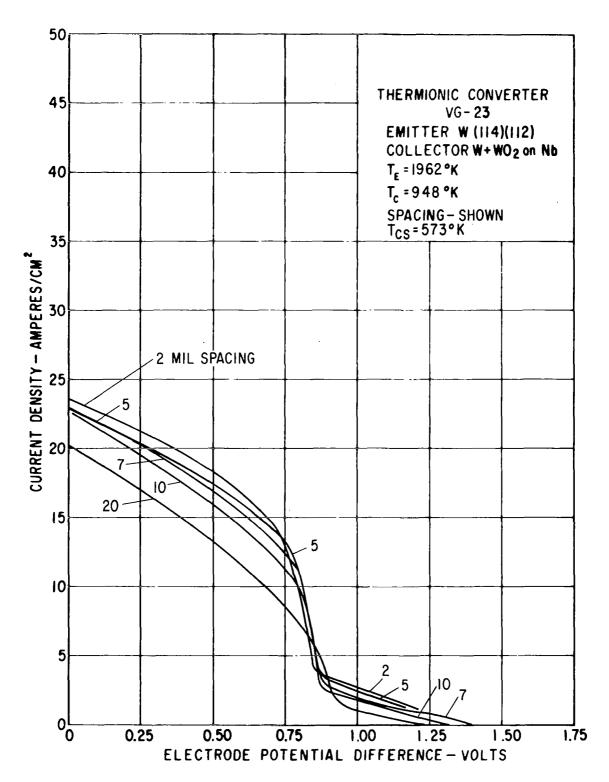
(d) Spacing, 10 mils; cesium temperature, $573^{\rm O}$ to ${<}613^{\rm O}$ K.

Figure 21. - Continued.



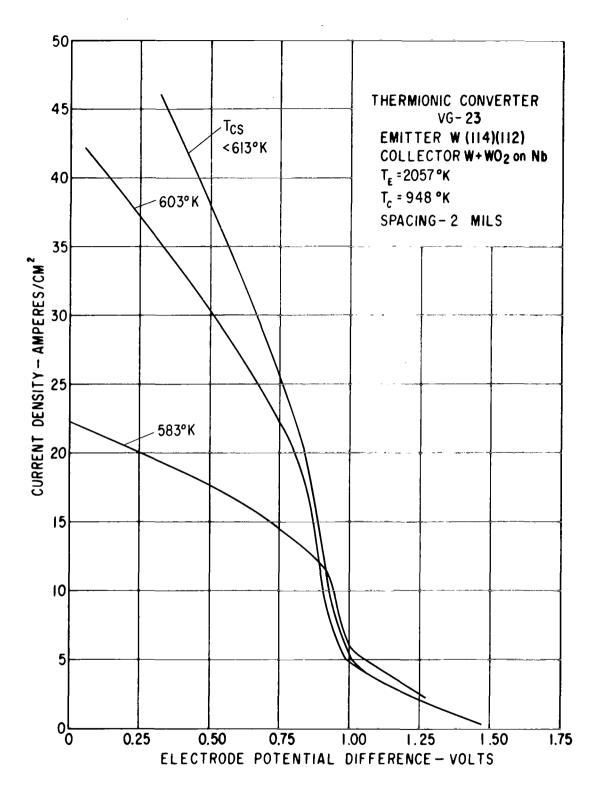
(e) Spacing, 20 mils; cesium temperature, 573° to $<613^{\circ}$ K.

Figure 21. - Continued.



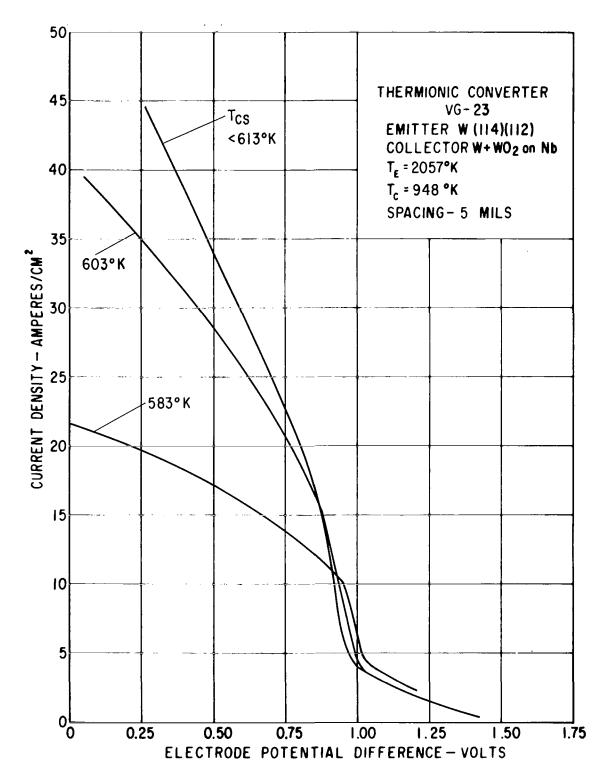
(f) Spacing, 2 to 20 mils; cesium temperature, $573^{\hbox{\scriptsize o}}$ K.

Figure 21. - Concluded.



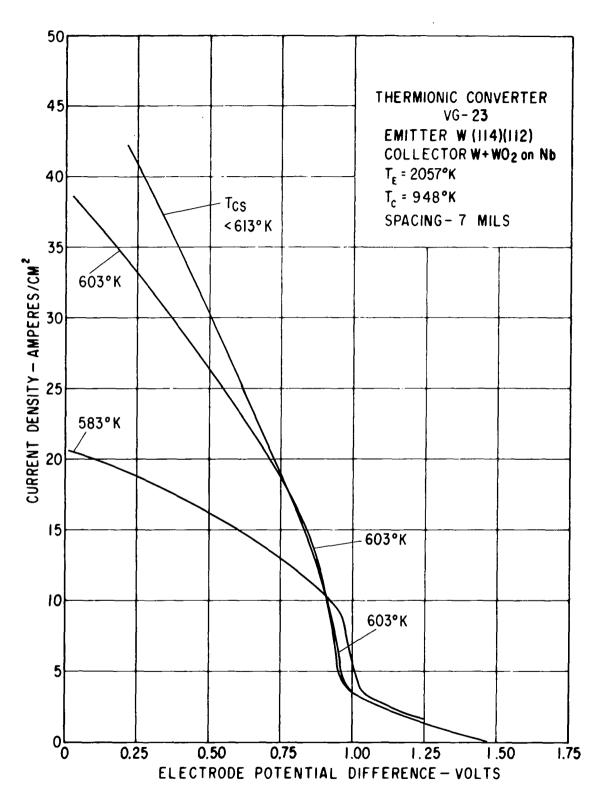
(a) Spacing, 2 mils; cesium temperature, $583^{\rm O}$ to ${<}613^{\rm O}$ K.

Figure 22. - Output characteristics of thermionic converter with W(112) to (114) emitter and collector of W + WO $_2$ on Nb. Emitter temperature, 2057 $^{\rm O}$ K; collector temperature, 948 $^{\rm O}$ K.



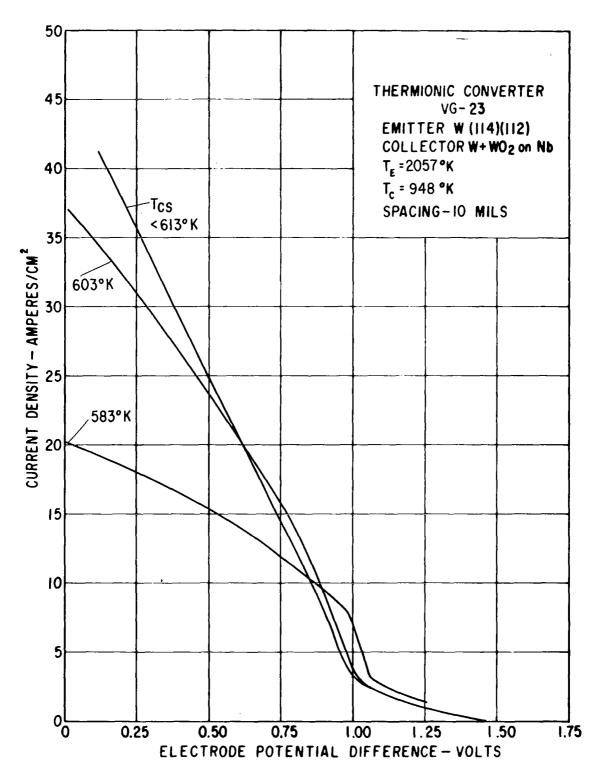
(b) Spacing, 5 mils; cesium temperature, $583^{\rm O}$ to ${<}613^{\rm O}$ K.

Figure 22. - Continued.



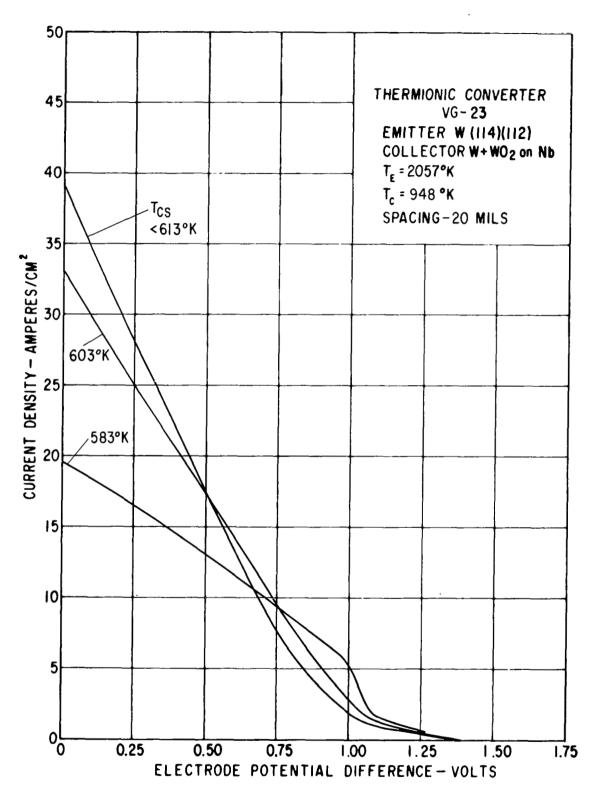
(c) Spacing, 7 mils; cesium temperature, 583° to $<613^{\circ}$ K.

Figure 22. - Continued.



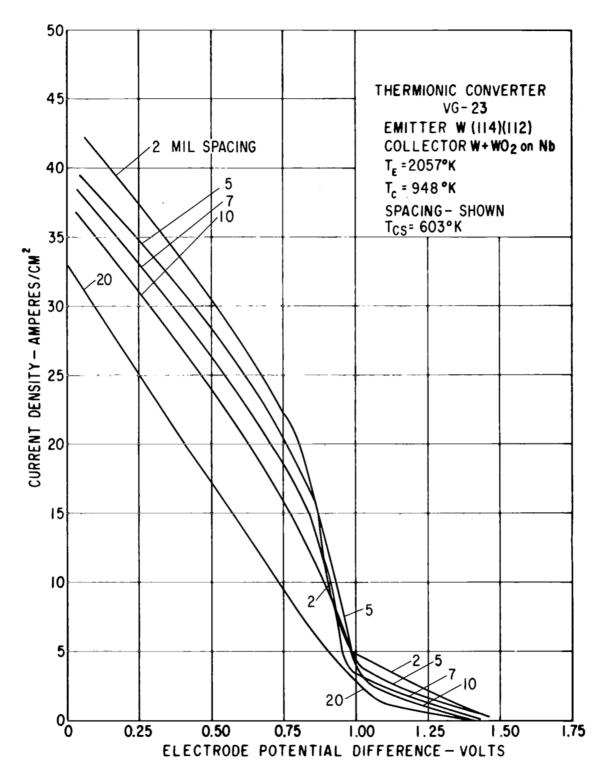
(d) Spacing, 10 mils; cesium temperature, 583° to $<613^{\circ}$ K.

Figure 22. - Continued.



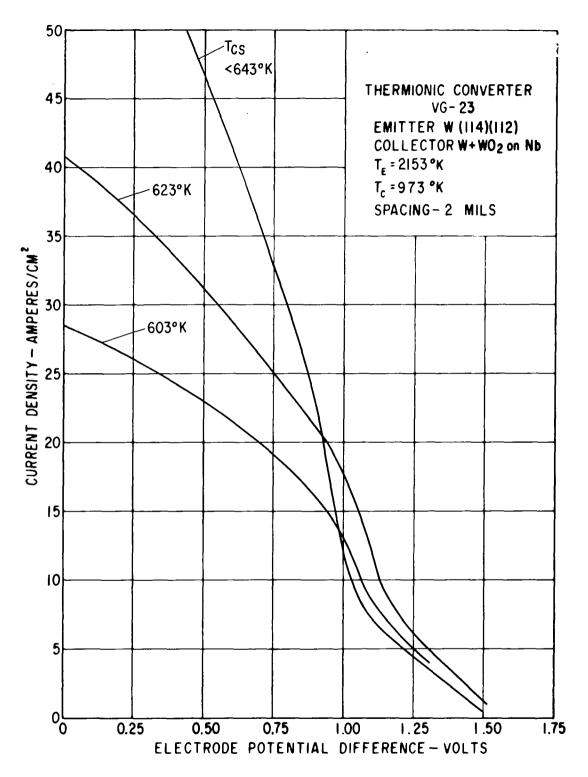
(e) Spacing, 20 mils; cesium temperature, $583^{\rm O}$ to ${<}613^{\rm O}$ K.

Figure 22. - Continued.



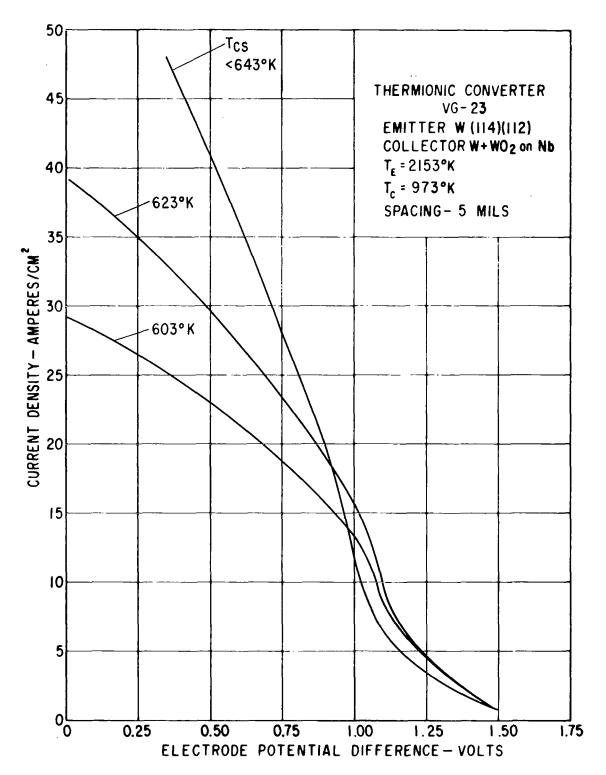
(f) Spacing, 2 to 20 mils; cesium temperature, $603^{\mbox{\scriptsize O}}$ K.

Figure 22. - Concluded.



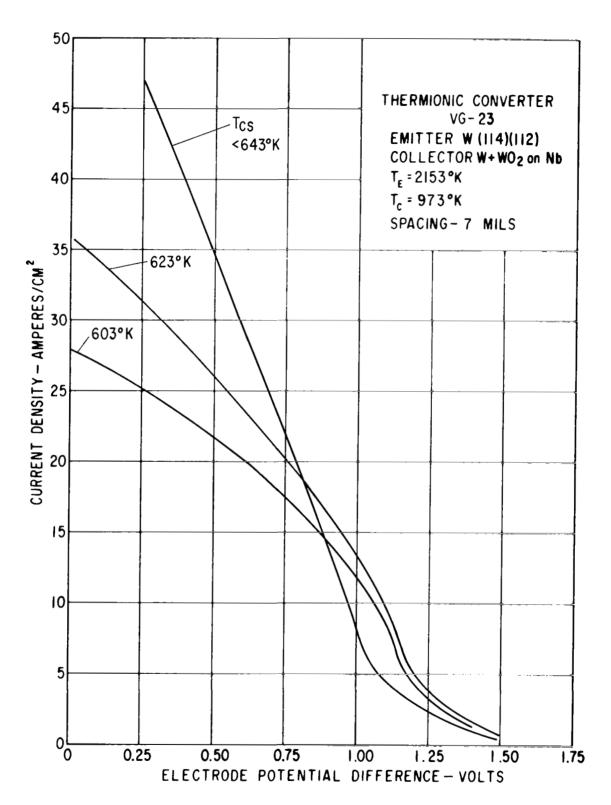
(a) Spacing, 2 mils; cesium temperature, 603° to <643° K.

Figure 23. - Output characteristics of thermionic converter with W(112) to (114) emitter and collector of W + WO $_2$ on Nb. Emitter temperature, 2153 $^{\rm O}$ K; collector temperature, 973 $^{\rm O}$ K.



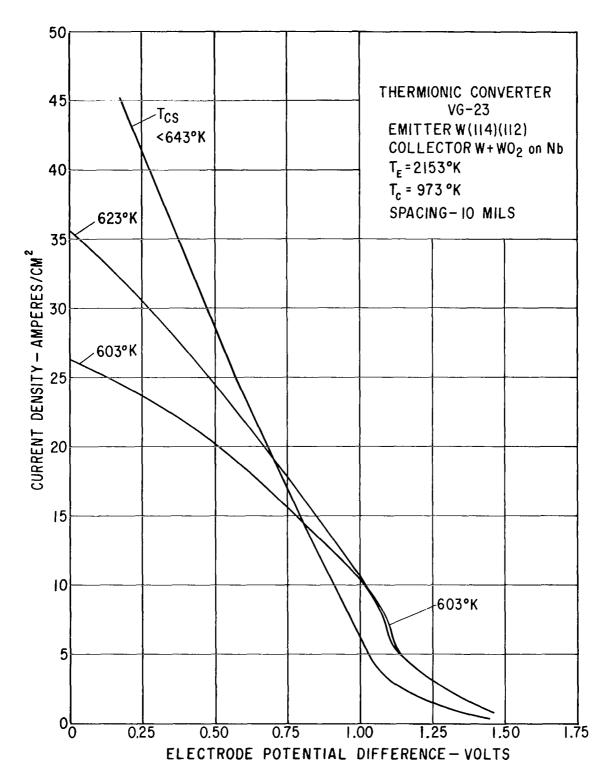
(b) Spacing, 5 mils; cesium temperature, 603° to <643° K.

Figure 23. - Continued.



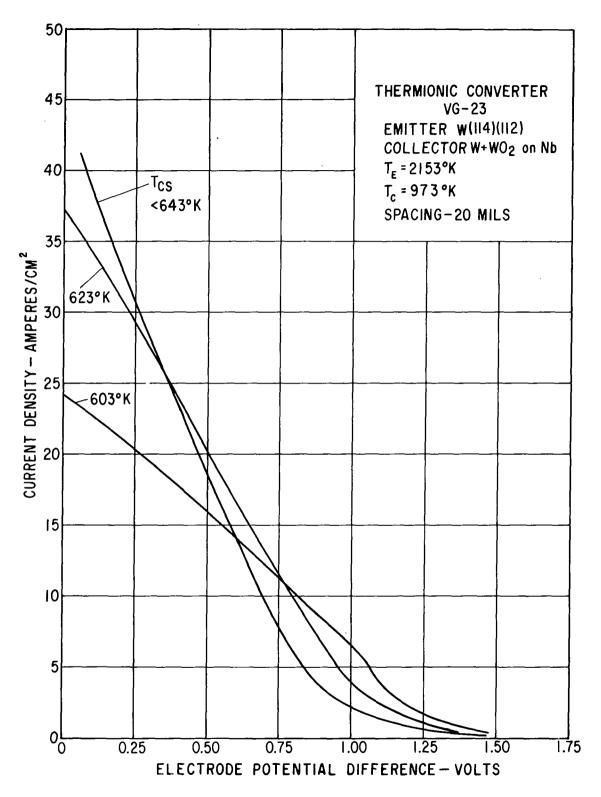
(c) Spacing, 7 mils; cesium temperature, $603^{\rm O}$ to ${<}643^{\rm O}$ K.

Figure 23. - Continued.



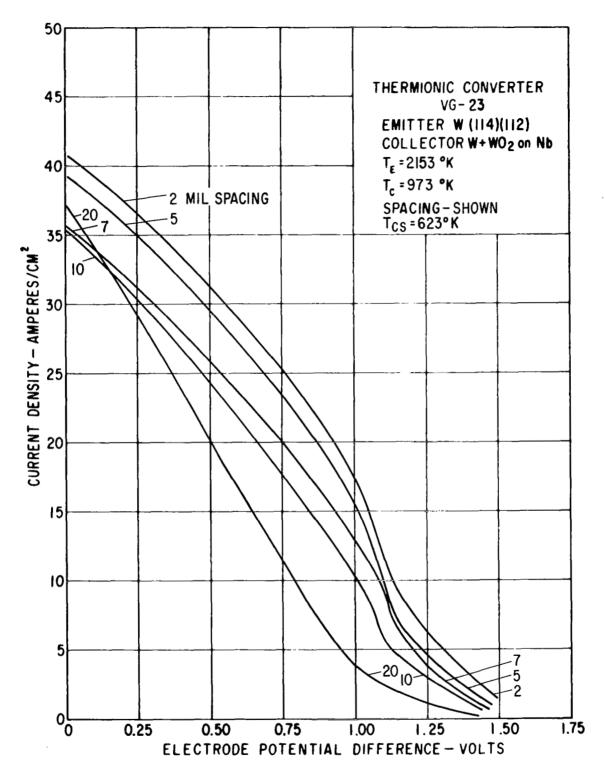
(d) Spacing, 10 mils; cesium temperature, $603^{\rm O}$ to ${<}643^{\rm O}$ K.

Figure 23. - Continued.



(e) Spacing, 20 mils; cesium temperature, $603^{\rm O}$ to ${<}643^{\rm O}$ K.

Figure 23. - Continued.



(f) Spacing 2 to 20 mils; cesium temperature, $623^{\rm O}$ K.

Figure 23. - Concluded.